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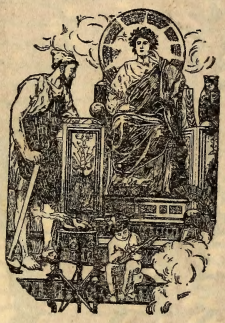

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SEMI-ANNUAL REPORT

on

Essential Oils,

Synthetic Perfumes, &c.

Published by

SCHIMMEL & Co.

(Fritzsche Brothers)

MILTITZ

near Leipzig

APRIL/OCTOBER 1918.

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List of abbreviations.

d = specific gravity.
$d_{20°}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d_{\frac{4°}{4°}}^{20°}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
$n_{D20°}$ = index of refraction at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Scientific and other Notes on Essential Oils.

Oil of Agonis flexuosa. When giving details on the prospects of producing eucalyptus oil in South Africa, R. H. Crozier[1]) describes the oil of the myrtle-willow *Agonis flexuosa*, Lindl. (N. O. *Myrtaceæ*), a low tree occurring abundantly in South-Western Australia. The oil resembles strongly eucalyptus oil and contains 62 to 72.2 per cent. of cineole, besides cymene, pinene, and traces of alcohols, esters, and phenols, but no aldehydes, free acids, nor phellandrene. The oil-yield amounted to 0.8 to 1.0 per cent. Owing to the abundant foliage it should be easy to collect enough distillation material from this tree.

Almond Oil, bitter. To judge by the samples submitted to our laboratories for analysis, especially of late, the trade in this article seems to be in a disgraceful state. It not only happens that ordinary, crude benzaldehyde, betrayed at once by its strong chlorine reaction, is sold as genuine oil, but there are people who do not even shrink from replacing it by the highly poisonous nitrobenzene. In one case, "bitter almond oil, I^a, pure", was composed of even parts of alcohol and nitrobenzene, whereas in another instance crude nitrobenzene had been supplied as *"Ol. amygdalarum verum sine acido hydrocyanico"*. As nitrobenzene smells somewhat like bitter almonds, the buyer often does not notice the fraud, which is all the worse, as oil of bitter almonds is frequently used in the household. How dangerous this substitute is, may be derived from a case of poisoning in Jena, where a woman used a teaspoonful of a 2 per cent. nitrobenzene solution for flavouring a cake, the partaking of which caused poisoning[2]). Fortunately, the effects were not severe, for the woman escaped with a transitory blue colouring of her face.

For curiosity's sake, we beg to mention one more sample of so-called bitter almond oil, sent us for inspection and which consisted chiefly of water, to which a small quantity of alcohol, perfumed with traces of bitter almond oil free from prussic acid, had been added.

Doubtless, the cyanogenic glucosides belong to the bodies which, from the phyto-physiological point of view, must be considered most interesting, since they yield the highly poisonous prussic acid. The presence of this acid has been proved in numerous plant destillates; some glucosides are the parent substances of benzaldehyde, which forms the main constituent of some essential oils, such as bitter almond and cherry laurel oils. Some of these bodies, hitherto inaccessible by means of synthesis, have been recently prepared artificially by E. Fischer and M. Bergmann[3]): — mandelonitrile glucoside, sambunigrine, and others.

The process of synthesis carried out was by no means simple. On shaking inactive ethylmandelate with acetobromoglucose and silver oxide, there results, in fairly good yields, the ethylester of tetracetyl-*d*-glucosido mandelic acid. This body is evi-

[1]) *S. Afr. Journ. of Industries*, December **1917**; *Perfum. Record* **9** (1918), 59. — [2]) *Pharm. Ztg.* **63** (1918), 311. — [3]) *Berichte* **50** (1917), 1047.

dently a mixture of two stereomerides which must be regarded as derivatives of *d*- and of *l*-mandelic acids. By means of ammonia, it passes over into a mixture of the glucosides of *d*- and *l*-mandelic amides. The lævorotatory derivative forms with pyridine a well-crystallizing compound that may be separated from the mixture by this means, whereas the *d*-stereomeride remains in the mother-liquor and may be isolated, after removing the pyridine, as an amorphous mass. Both amides are easily transformed, by aid of acetic anhydride and pyridine, into tetracetyl derivatives which on heating with phosphorus oxychloride yield the two well-crystallizing tetracetyl mandelonitriles. One of these is identical with the well-known tetracetyl derivative of the old mandelonitrile glucoside, the other is also formed on treating sambunigrine with pyridine and acetic anhydride. The elimination of the four acetyl groups, so easily performed with the ordinary glucosides, is here particularly difficult, since the cyanogen radicle is rather sensitive towards alkalies or barium hydroxide. A satisfactory yield of the glucosides is only obtained when performing the saponification with methylalcoholic ammonia. These preparations, however, are not the pure mandelonitrile glucosides, but a mixture of both, which was not surprising, since Caldwell and Courtauld[1]) have found that *l*-mandelonitrile glucoside is partly rearranged into the so-called prulaurasine by means of very diluted cold bases. Yet it was possible to split up the mixture into its two components by crystallization.

Mandelonitrile glucoside has been first prepared by E. Fischer[2]) by partial hydrolysis of amygdaline with yeast extract. Fischer, too, gave then its structural formula being hitherto in use, and pointed out that it possibly occurred naturally. He intended to identify it with the amorphous amygdaline (laurocerasine), but did not carry out his intention. Only years later, in 1906, Hérissey[3]) succeeded in isolating, from fresh cherry laurel leaves, a crystallized amygdaline instead of the amorphous laurocerasine, which he termed "prulaurasine" and found to be a homogenous isomeride of mandelonitrile glucoside. A short time before, Bourquelot and Danjou[4]) had prepared crystallized sambunigrine from elder leaves and considered it also an isomeride of mandelonitrile glucoside. Furthermore, Hérissey[5]) found mandelonitrile glucoside in the fresh branches of *Prunus Padus*. Caldwell and Courtauld[6]) found about the same time, that mandelonitrile glucoside is transformed into prulaurasine by means of very diluted aqueous baryta or ammonia solution. They recognized clearly the relations existing between the three glucosides, the oldest of which they termed quite correctly *l*-mandelonitrile-*β*-glucoside, whereas sambunigrine was considered to be the *d*-isomeride, and prulaurasine a mixture of both. This view was confirmed by Bourquelot and Hérissey[7]) since they obtained, by action of hydrochloric acid, *l*-mandelic acid from the old mandelonitrile glucoside, and the *d*-acid from sambunigrine. Furthermore, they found sambunigrine to be transformed into prulaurasine by means of baryta water.

This extremely rapid transfiguration, or the very easy partial racemisation of both mandelonitrile glucosides by aid of bases is striking and may be connected with some change in their structure.

The behaviour of both mandelamido glucosides towards emulsin is remarkable. Whereas the nitriloglucosides ar hydrolyzed rapidly, by that enzyme, only *l*-mandelamido glucoside undergoes that reaction.

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[1]) *Journ. chem. Soc.* **91** (1907), 671; *Report* October **1907**, 12, 13. — [2]) *Berichte* **28** (1895), 1508. — [3]) *Journ. de Pharm. et Chim.* VI. **23** (1906), 5; *Report* April **1906**, 107. — [4]) *Journ. de Pharm. et Chim.* VI. **22** (1905), 219, 385; *Report* April **1906**, 105. — [5]) *Journ. de Pharm. et Chim.* VI. **26** (1907), 194; *Arch. der Pharm.* **245** (1907), 641; *Report* April **1908**, 13. — [6]) *Journ. chem. Soc.* **91** (1907), 671; *Report* October **1907**, 12, 13. — [7]) *Journ. de Pharm. et Chim.* VI. **26** (1907), 5; *Report* October **1907**, 12.

The properties of the different bodies were: — the ethyl ester of tetracetylglucosido-*d*+*l*-mandelic acid crystallizes from alcohol and melts indistinctly between 102 and 109°. Inactive mandelate having served as starting material, it was to be expected that this preparation was a mixture. The glucoside of mandelic amide, obtained from the ester by action of methylalcoholic ammonia, is as well as the ester a compound of two isomerides which may be separated by crystallization from pyridine. The glucoside of *l*-mandelic amide presents itself as a viscid colourless syrup, drying up in a dessiccator into a brittle, glass-like mass. Emulsin splits it easily into sugar and *l*-mandelic amide. The mandelic amide glucoside is easily transformed into a pyridine compound. The tetracetate of the *l*-glucoside melts at about 161°. The *d*-glucoside of mandelic amide could neither be obtained in the crystallized state; its tetracetate, melted at 136 to 137°. The tetracetates of mandelic nitrile glucoside showed the melting points: — *d*-isomeride, 125 to 126°, *l*-isomeride, 139 to 140°.

In order to compare them with the synthetic preparations, the authors have prepared the acetates of *l*-mandelic nitrile glucoside and of sambunigrine. The former compound was obtained by action of yeast extract on amygdaline. The acetates of the natural as well as of the synthetical bodies showed the same melting points. *l*-Mandelonitrile glucoside, obtained by Fischer and Bergmann by saponification of *l*-mandelonitrile glucoside tetracetate with aid of methylalcoholic ammonia, showed an optical rotation of — 51.9° to — 54.5°, whereas Hérissey states — 52.6° and 54.6° for his prulaurasine from cherry laurel leaves, and Caldwell and Courtauld — 52.7°.

Fischer and Bergmann have not decided the question whether prulaurasine is simply a mixture of *d*- and *l*-mandelic nitrile glucosides, or whether under certain conditions it may occur as uniform body (by partial racemisation). However, they succeeded in splitting up their preparation, by crystallization, into two pure glucosides. They obtained, furthermore, from prulaurasine, by crystallization from amyl alcohol and benzene, sambunigrine of the correct melting point; the tetracetate also showed the properties expected; the mother liquor contained the glucoside of *l*-mandelic nitrile, which was identified by its constants and by its tetracetate.

Oil of Alpinia nutans. The root of *Alpinia nutans,* Roscoe, a Zingiberacea occurring in tropical Asia, contains a volatile oil, of the composition and properties of which, however, only very little is known. More is known about the oil of the leaves, which K. Kafuku[1]) has obtained in a yield of 0.053 per cent.; $d_{19°}$ 0.9301, α_D + 38.4°, n_{D200} 1.4750, sapon. v. 9.88, sapon. v. after acetylation 36.1. The oil contains more than 30 per cent. *d*-camphor, 17 per cent. *d*-camphene[2]), besides cineole, an ester of cinnamic acid, and probably also a sesquiterpene, a high-boiling phenol, and limonene.

Ammoniacum Oil. F. W. Semmler has published his paper on aforesaid oil (discussed in our *Report* October 1917, 20) in community with P. Roenisch, in a second periodical[3]).

Oil of an Andropogon Species. In our last *Report* (p. 4) we dealt with an oil distilled by us, for sampling purposes, from the herb and the roots of *Andropogon Gryllus,* L., or *A. Ischœmum,* Thunb. In the meantime, we prepared the same oil from another small sample of the same material and we communicate hereunder the results obtained. The yield was more satisfactory than at first, amounting to 1.0 per cent.

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[1]) *Kogyo-Kwagaku-Zasshi* (*J. chem. Ind.*, Tokyo) **20** (1917), 349; *Journ. Soc. chem. Industry* **36** (1917), 905. — [2]) The absfract cites, probably by mistake, camphane. — [3]) *Berichte* **50** (1917), 1823.

The colour was again pale yellow, the smell, too, of the same unpleasant character as at first. The acetylation value of the oil indicated only a low content of alcoholic constituents, corresponding to an amount of only 10.5 per cent. alcohol $C_{10}H_{18}O$.

The latter roots were forwarded to us from the Government factory for cleansing facilities at Kevevára, Hungary; here the roots are dug out in enormous quantities and turned into brushes.

Angelica Oil. As to the cultivation of angelica, see page 78 of this *Report*.

Angophora Oils. *Oil of Angophora Bakeri.* Leaves collected in the neighbourhood of Paramatta, Australia, from this myrtacea yielded, according to Baker and Smith[1]) 0.31 per cent. volatile oil; d 0.8719, $\alpha_D + 35.6°$, n_D 1.4660. The following bodies proved to be present: — α-pinene, geraniol, geranyl acetate and valerate, a sesquiterpene, amyl acetate, and a volatile aldehyde. The content of α-pinene amounted to 80 per cent.

Oil of Angophora melanoxylon, R. T. Baker. The leaves of this species yielded 0.19 per cent. oil with the constants: — d 0.8809, $\alpha_D + 24.9°$, n_D 1.4678. Its composition was similar to that of the above-mentioned oil.

Oil of an Angophora species (?). The oil of a still unnamed species also contained pinene, geranyl acetate, and valerate; d 0.8703, $\alpha_D + 36.3°$, n_D 1.4669.

Unfortunately, the abstract does not mention where the original paper was published and how the constituents of the oils were identified.

Anise Oil. Small quantities of anise are grown in Cyprus[2]), the exports amounting in the last years to 1000 to 2000 cwt. annually. In 1915, 1112 cwt., valuing 1823 £ were shipped to Egypt. A sample was investigated at the Imperial Institute, London, and yielded on steam-distillation 2.8 per cent. of a faint yellow oil: — $d_{15°}$ 0.990, $\alpha_D \pm 0$, $n_{D24°}$ 1.557, soluble in 2.8 vols. 90 per cent. alcohol, solidif. point 17.5°.

Oil of Artemisia annua. In page 4 of our last *Report* we mentioned, following a description of this oil by Y. Imada[3]), as constituents cineole and another substance $C_{10}H_{16}O$. As we cull from another abstract of the same paper, the presence of cineole was established by oxidation into cineolic acid and by preparing the iodole addition compound. The oil, a light yellow liquid of camphoraceous smell, had the constants: — acid v. 2.1, sap. v. 36.4, sap. v. after acet. 66.36, methoxyl v. 0.

The second body $C_{10}H_{16}O$ has been investigated by Asahina and Yoshitomi[4]) and termed "artemisia ketone". They heated the semicarbazone (m. p. 95 to 96°) with concentrated hydrochloric acid under a reflux condenser for six hours; the regenerated ketone was inactive and showed b. p. 182°, $d^{14°}_{4°}$ 0.8906, $n_{D18°}$ 1.4695. It contained two double linkings and yielded in consequence, when reduced according to Fokin-Willstätter, a tetrahydro derivative $C_{10}H_{20}O$, tetrahydro artemisia ketone, b. p. 173°; $d^{19°}_{4°}$ 0.8262; n_D 1.42425; m. p. of the semicarbazone 134 to 135°. It seemed to be of aliphatic structure.

A further constituent of the oil was *l*-camphor, m. p. 175°; m. p. of the semicarbazone 237°.

The properties of the original oil examined by the authors were: — $d^{16°}_{4°}$ 0.9080; α_D 16.19° (nothing as to the direction of rotation is stated), acid v. 1.82, ester v. 34.58, ester v. after acet. 63.54.

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[1]) *Perfum. Record* **9** (1918), 22. — [2]) *Bull. Imp. Inst.* **15** (1917), 300. — [3]) *Yakugakuzasshi; Chemist and Druggist* **89** (1917), 376. — [4]) *Journ. pharm. Soc. Japan* 1917, **1** (no. 424?); *Chemist and Druggist* **89** (1917), 746. — *Yakugakuzasshi* **1917**, No. 524; *Apotheker-Ztg.* **32** (1917), 620. — *Perfum. Record* **8** (1917), 353.

Oil of Asparagus Sprengeri. F. Elze[1]) isolated an essential oil of almost narcotic smell from the small, pale rose flowerets of *Asparagus Sprengeri*, Regel, *(Liliaceæ)*, commonly known as smilax. This oil of intense odour, recalling that of the fatty aldehydes, can be obtained by extracting the flowerets with an easily volatile solvent, removing this and making the extract soluble by means of alcohol. On being treated with an acetic semicarbazide solution, it yielded a distinct precipitate of semicarbazone crystals, but the quantity was too small to permit of a closer investigation. It is possible to obtain a similar volatile oil by distillation with steam, but the fact that its odour is less intense and not so fine as that of the extracted product seems to indicate that it is partly decomposed by the steam.

Balm Oil. As to the cultivation of balm, see page 79 of this *Report*.

Bay Oil. According to Tempany[2]), bay oil distilled in Montserrat in 1916 had the following properties: — d 0.926 to 0.940 (determined at 30 to 31°, corresponding to 0.938 to 0.952 at 15°), phenol content 46.5 to 54 per cent. The latter value is rather low, as Tempany remarks, and is probably due to the extremely damp weather. There was no relation observable either between phenol content and distillation period or between the former and oil yield.

Oil of Birch buds. H. von Soden and F. Elze[3]) had found a sesquiterpene alcohol $C_{15}H_{24}O$, termed by them "betulol", to be a component of birch bud oil. Nothing was hitherto known as to its structure. F. W. Semmler, K. G. Jonas and W. Richter[4]) show now that betulol belongs to the class of bicyclic sesquiterpene alcohols with terpene structure. The constants found by Semmler and his collaborators as well as by von Soden and Elze, and by ourselves are compiled in the table below. Semmler isolated the betulol from an oil originating from us, by means of V. Paolini's[5]) method of preparing the acid phthalic ester, a resinous, viscid mass, yielding pure betulol on saponification.

The constants of betulol.

	B. from birch bud oil purified by aid of the acid phthalic ester (Semmler)	B. from the crude oil by saponification (Semmler)	B. after von Soden and Elze	B. purified by means of the acid phthalic ester (Schimmel & Co.)
Boil. point	157 to 158° (13 mm.)	156 to 160° (13 mm.)	138 to 140° (4 mm.)	158° (7 mm.)
Spec. grav.	$d_{16°}$ 0.977	$d_{19°}$ 0.9765	$d_{15°}$ 0.975	$d_{15°}$ 0.9777
Opt. rot.	α_D — 26° 30′	α_D — 26° 36′	α_D — 35°	α_D — 19°46′
Refraction	$n_{D16°}$ 1.5150	$n_{D19°}$ 1.5149		$n_{D20°}$ 1.51385

According to Semmler, the acetate of betulol has the b. p. 158 to 165° (10 mm.); $d_{20°}$ 0.9854; α_D — 12°; $n_{D20°}$ 1.4962. On saponification, unchanged betulol is regenerated. Von Soden and Elze found for the acetate: — b. p. 142 to 144° (4 mm.); $d_{15°}$ 0.986.

On comparing the constants of betulol with those of β-santalol (b. p. 160 to 168° [10 mm.]; $d_{20°}$ 0.973; α_D — 21°; $n_{D20°}$ 1.5097), the alcohol manifests its ranging with the bicyclic sesquiterpene alcohols of the terpene type. However, betulol differs from β-santalol by its low boiling point and its higher refraction.

In order to prove the presence of the two double bonds, Semmler reduced betulol, $C_{15}H_{24}O$, dissolved in absolute ether, by means of platinum and hydrogen into saturated

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[1]) *Chem. Ztg.* **41** (1917), 842. — [2]) *Perfum. Record* **8** (1917), 160. — [3]) *Berichte* **38** (1905), 1636; *Report* October **1905**, 13. — [4]) *Berichte* **51** (1918), 417. — [5]) *Atti R. Accad. dei Lincei*, Rome (5) **20**, I (1911), 765; *Chem. Zentralbl.* **1911**, II. 690.

tetrahydrobetulol $C_{15}H_{28}O$; b. p. 153 to 158° (14 mm.); $d_{18°}$ 0.9415; α_D — 6° 48′; $n_{D18°}$ 1.4908. In the course of this reduction, partial dehydration took place, with formation of bicyclic tetrahydrobetulene $C_{15}H_{26}$; b. p. 118 to 120° (11 mm.); $d_{18°}$ 0.8737; α_D — 3°; $n_{D18°}$ 1.4744. By treatment with phosphorus pentachloride, in light petroleum solution, betulol yields easily betulyl chloride; b. p. 160 to 170° (11 mm.); $d_{21°}$ 1.0145; which when dissolved in absolute alcohol and dropped on heated metallic sodium passed over into an unseparable mixture of bicyclic and tricyclic betulene. On treating betulyl chloride with an aqueous paste of calcium hydroxide, there resulted a tricyclic betulol, in addition to a bicyclic dehydrosesquiterpene $C_{15}H_{22}$ and probably some tricyclic dehydrosesquiterpene. Tri*cyclo*betulol, $C_{15}H_{24}O$, forms crystals of silky lustre, m. p. 147 to 148°. The same alcohol results, in addition to dehydrobetulene, on treating the chloride with alcoholic potash, but the yield is far lower. The acetate of tri*cyclo*betulol had the constants: — b. p. 170 to 176° (13 mm.); $d_{22°}$ 1.0290; α_D + 10°; $n_{D22°}$ 1.5046.

Oil of Buchu leaves. On page 28 of our October *Report* of 1913, we discussed a notice from *The Chemist and Druggist*, according to which the gathering and the sale of buchu leaves in the Cape Colony were going to be regulated by law. This seems to have been done meanwhile[1]). The territory and the time of collecting have been defined and a certain tax has to be paid for a permit. The consequence of this measure is said to be a decrease of the export last year, but it must be taken into consideration that the United States, formerly the chief consumers, now show far less interest for this drug. They employ a native substitute, as the price of buchu leaves from *Barosma betulina* is too high.

The exports of buchu leaves from the Cape Colony in the years from 1900 to 1916 were as follows: —

year	quantity exported lbs.	value £	average price d	year	quantity exported lbs.	value £	average price d
1900	229 197	4367	4	1909	264 126	9 666	8
1901	220 306	5665	6	1910	273 325	24 228	21
1902	161 570	4775	7	1911	212 082	29 647	33
1903	262 454	8055	7	1912	223 021	38 264	41
1904	251 635	2498	6	1913	163 812	32 471	46
1905	231 122	5505	5	1914	149 113	27 558	44
1906	290 106	7769	6	1915	157 061	23 767	36
1907	291 334	9201	7	1916	130 794	21 685	39
1908	243 422	7248	7				

These figures do not refer only to the leaves of *Barosma betulina*, but also to those of *B. crenulata* and *B. serratifolia*.

Oil of Callitris rhomboidea. As Puran Singh[2]) reports, the leaf oil of the Oyster Bay pine, *Frenela (Callitris) rhomboidea*, is particularly suited for scenting soaps. The tree was cultivated in the Nilgiris as far back as 1885, and at present about 130 acres are planted with that conifer. The fresh leaves yielded in November 0.039 per cent. oil of the properties: — $d_{16°}$ 0.8710, α_D — 27.6°, $n_{D18°}$ 1.4695, ester v. 51.14, sap. v. 52.3, sap. v. after acetyl. 59.8 (corresponding to 2.09 per cent. free alcohols calculated as

[1]) E. P. Phillips, *South African Journal of Industries*, September 1917; *Chemist and Druggist* **110** (1918), 31. — [2]) *Perfum. Record* 8 (1917), 304.

geraniol, 17.28 per cent. total alcohols, and 17.85 per cent. geranyl acetate). The oil was soluble in 0.75 vol. 90 per cent. alcohol and 21.5 vols. 80 per cent. alcohol.

Baker and Smith[1]) found the following constants for the oil of *Callitris rhomboidea*: — $d_{22°}$ 0.8826, α_D — 19.2°, n_{D25} 1.4747. The ester content, calculated as geranyl acetate, amounted to about 30 per cent.

Baker and Smith, in corresponding with the editor of the *P. E. O. R.*[2]), state quite correctly that the Oyster Bay pine is not identical with *Frenela rhomboidea,* but with *F. Tasmanica.* Besides, the term *Frenela* is hardly correct in the light of our present knowledge, since Mirbel coined the term *Frenela* much later after Ventenat established the genus *Callitris.* The latter term, therefore, must be applied.

Baker and Smith consider it a pity that *C. rhomboidea* and not *C. Tasmanica* has been introduced into India, as the yield of oil is about six times as great, while the ester content is more than double that in the oil of *C. rhomboidea.*

Camphor Oil. The camphor production in Formosa is estimated at 11 600 000 lbs.[3]) to the value of $ 3 200 000, in 1917. All possible measures have been taken on this island in order to foster the cultivation of the camphor tree.

In 1916 (fiscal year?), 528 000 lbs. of camphor per month were exported to the United States. These monthly quantities have risen to 1 000 000 lbs. after April 1st, 1917, owing to a fresh agreement between the Japanese Government and American merchants.

As per a later report[4]), the camphor production in Formosa for the fiscal year ending on April 1st, 1918 may be estimated at 7 056 720 lbs., of which 4 350 000 lbs. are destined for the American celluloid factories. Unfavourable weather might reduce the output to 1 320 000 lbs., in which case only 594 000 lbs. would go to America.

We gather from another source[5]) that the imports of camphor into the United States rose from 4.5 to 4.9 and 8.6 million lbs., respectively, in the years 1914, 1915 and 1916. It is worth noticing that the imports of refined camphor went up from 1 to 1.2 and 3 million lbs., respectively. Needless to say that a good share was used for war purposes, but the enlarged production of films, windows for motor-cars, and celluloid and fiberoid, generally speaking, will likewise have caused this increase.

After having thoroughly gone into the manufacture of synthetic indigo, the United States also wish to replace the import of camphor from Japan by the production of artificial camphor at home. In order to cover the total requirements of the American industry, more than 100 000 barrels of oil of turpentine would be required for this purpose, *i. e.* as much as the whole stocks available in Savannah.

According to another notice[6]), the camphor exports from Japan to America in 1914 to 1917 amounted to:—

	crude camphor	refined camphor
1914	3 488 271 lbs.	1 054 177 lbs.
1915	3 712 328 „	1 205 287 „
1916	5 654 281 „	3 011 072 „
1917	5 512 807 „	3 108 240 „

As regards the camphor production in Japan proper, it is estimated at 1 627 422 kin for the last fiscal year, 1916/17, an increase of 26 607 kin as compared with 1915/16[7]). The yield in Formosa increased still more considerably; *viz.,* by 394 561 kin, the total being 5 017 743 kin.

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[1]) *A Research of the Pines of Australia,* Sydney **1910,** 227; *Report* April **1911,** 29. — [2]) *Perfum. Record* **9** (1918), 108. — [3]) *Journal of Commerce,* May 30th, 1917; *Chem. Industrie* **40** (1917), 331. — [4]) *Chemist and Druggist* **89** (1917), 765. — [5]) *Chem. Ztg.* **42** (1918), 71. — [6]) *Oil, Paint and Drug Reporter; Perfum. Record* **9** (1918), 108. — [7]) *Chem. Industrie* **40** (1917), 293.

The production of camphor oil, in 1916/17, was 3210494 kin in Japan (+ 209073 kin as compared with 1915/16) and 7827560 kin in Formosa (+ 946328 kin as compared with 1915/16). The export figures in 1000 yen run as follows: —

	1914	1915	1916
British-India	907	1343	1416
England	378	322	639
France	264	530	380
Germany	290	—	—
United States	765	1035	2654
Australia	110	170	93
other countries	360	480	572
	3074	3880	5754

According to the *"Journal of Commerce"* of April 21st, 1916[1]), the shipments of crude camphor from Japan have been stopped without any official statement of the reasons. Refined camphor, on the contrary, is further exported. It therefore seems to be the idea of the Japanese Government to refine the product in future exclusively in Japanese factories, so that the country profits. The most important producer, Formosa, exported for 3.96 million yen during the nine first months of 1916, against 2.51 in the year before. Japan's total production is estimated at 11 million lbs. The exports of camphor[2]) in the last years was: —

1913	1463 tons,	2.24	million yen
1914	1815 „	2.78	„ „
1915	2292 „	3.48	„ „
1916	3400 „	6.29	„ „

The Monopoly Bureau raised the price four times, in 1916, from 74 yen per 100 kin in the beginning to 87 yen at the close of the year.

According to the British attaché at Yokohama[3]), the erection of a camphor refining plant in Formosa is intended with a view to refine the whole production of the island. A limited company with a capital of 1 million dollars will be founded for the purpose. So far, all the Formosa camphor was exported in a crude state, excepting the quantities refined in Kobe. This year's camphor crop (1916?)[4]) came up to 11616000 lbs., representing a value of 3165000 dollars.

In Formosa, everything is done to foster camphor tree planting. In former years many young trees have been planted, from which it will be possible to get a benefit during the next 30 years to come. But on the other hand, the old trees disappear gradually, so that one has misgivings sometimes as to the future of the camphor industry.

China's camphor exports have decreased again, in 1915[5]). They amounted to 1318 piculs to the value of 98075 Haikwan taels, as compared with 1810 piculs to the value of 131574 Haikwan taels in the previous year. The destinations were as follows: —

destination:	1914 piculs	1914 Haikwan taels	1915 piculs	1915 Haikwan taels
United States	542	43355	175	14950
British India	111	8850	44	3759
Hongkong	1148	78773	1084	78167
France	—	—	10	854

[1]) L. Ulrich, *Der Wirtschaftskrieg, 3. Abtlg. Japan*, Jena 1917, S. 95. — [2]) It is not to be seen whether these figures apply to crude or refined camphor. — [3]) *Journ. of Ind. and Engin. Chemistry* 9 (1917), 905. — [4]) Most likely the fiscal year ending March 31st, 1917, is meant. — [5]) *Perfum. Record* 8 (1917), 88.

Owing to a system of exploitation, regardless of the future, such as has been carried out in the Foochow district during the ten last years, the camphor business has almost come to a standstill. Previous to 1902, the production showed a continuous increase and in 1907 amounted to 2 600 000 lbs., afterwards it went down rapidly and barely totalled 60 000 lbs. last year[1]).

In one of our former *Reports*, we discussed a treatise by B. J. Eaton[2]) on the production of camphor oil in the Federated Malay States, and later on we briefly reverted to the matter[3]). We now have before us again an article on the subject, entitled "Camphor oil from the Federated Malay States and Mauritius"[4]), but the oils mentioned therein are not normal, like those obtained in Formosa from camphor wood, having been distilled from the leaves and hence being characterized, as it is known, by the absence of safrole.

It has been found out that the leaves of the camphor tree contain far more volatile constituents than the branches, deprived of their leaves. The leaves of trees 2 years old, *e. g.*, yielded 1.4 to 1.6; those of trees 4 years old, 1.3 to 1.7 per cent. of distillate, whereas the figures for the branches were 0.10 to 0.25 and 0.13 to 0.22 per cent., respectively.

In 1913, the Imperial Institute received a sample of camphor oil of a pale yellow colour and which had deposited considerable quantities of camphor. In order to free the oil from the deposit, it was repeatedly cooled down to $-12°$ and filtered. After having been treated in this way, the oil showed $d_{15°}$ 0.913 and $\alpha_D + 41°1'$. The components boiling between 155 and 195° contained cineole (4.3 per cent. of the original oil) and those boiling between 195 and 225°, camphor. The total quantity of camphor contained in the original oil was 30.5 per cent. There was no safrole present in the fractions boiling from 195 to 225°.

Camphor trees have been planted too in Mauritius, where they prosper, but so far camphor has only been obtained there on an experimental scale. In 1912, the Imperial Institute received from Mauritius samples of camphor oil with the following properties: — $d_{15°}$ 0.90 to 0.925, $\alpha_D - 6°20'$ to $-21°5'$, cineole content 65 to 72 per cent. (determined by the resorcinol method). As the oils had such a high percentage of cineole, a further five similar samples were investigated. There were two oils from branches, one from leaves, one from wood and one from roots. They had all been distilled in a copper still, except that from roots, of which only half came from a copper still, the other half from a wooden one.

The leaf oil had been obtained from fresh leaves at different stages of maturity and from small twigs taken from very old trees. In January, the yield was 0.75 to 0.92 per cent., in the months of March till May, 0.48 to 0.61 per cent., and in June and July, 0.71 to 1.1 per cent. Leaves without stalks yielded 1.24 per cent. of oil, in July. It was impossible to obtain solid camphor from the leaves.

Roots yielded 2.97 per cent. of oil, branches from very old trees, 0.60 per cent. of oil; branches from a tree growing near a river contained only 0.21 to 0.31 per cent. of oil. From wood, 0.77 per cent. of oil were obtained.

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[1]) *Der Neue Orient* **3** (1918), 45. — [2]) Camphor from *Cinnamomum Camphora* (the Japanese camphor tree), cultivation and preparation in the Federated Malay States. Department of Agriculture. Bulletin No. 15, February 1912; *Report* October 1912, 28. — [3]) *Bull. Imp. Inst.* **11** (1913), 46; *Report* October **1913**, 34. — [4]) *Bull. Imp. Inst.* **14** (1916), 577.

The various oils showed the following properties: —

	d_{150}	α_D	components absorbed by resorcinol
1. Oil from leaves . . .	0.9162	$-18°38'$	56 per cent.
2. „ „ roots . . .	0.9508	$+13°36'$	38 „ „
3. „ „ branches . .	0.9143	$-15°22'$	54 „ „
4. „ „ „ . .	0.9243	$-11°37'$	—
5. „ „ wood . . .	0.9164	$-11°26'$	—

The oil derived from roots contained 6 per cent. of camphor and considerable quantities of safrole. The oils numbers 1, 3, 4 and 5 seemed to be of very similar composition. It is evident that all these oils differ in their properties from normal distillates, which deposit solid camphor. The wood ought to furnish an oil similar to the normal Formosa camphor oil. However, even on repeating the experiments, oils of different properties resulted.

So far, no explanation has been found for the abnormal properties of the oils. The trees all seemed to belong to the right species, *Cinnamomum Camphora,* Nees; however, on botanical examination trifling differences were stated. Perhaps we have here to deal with a variety containing little camphor; it is said that in Formosa too similar trees occur.

We beg to recall the fact that the so-called Yu-Ju oil, described by Nagai[1]), also showed a great resemblence to camphor oil, but differed from it by not depositing any solid camphor. The Yu-Ju tree looks so much like the camphor tree that it can only be distinguished from it by the smell of the wood. It is still unknown to which botanical species it belongs. The main constituent of the oil is cineole.

Owing to the high price of camphor in the last years, Florida has shown a keener interest in the cultivation of the camphor tree, starting fresh plantations or increasing the existing ones. The method of exploitation of the trees in Florida differs greatly from that in Japan and Formosa; it only pays when carried out on a large scale. S. C. Hood[2]) thought it advisable, therefore, to publish the results of his investigations of the causes of the varying yields of camphor obtained from the Florida trees, made in the years from 1907 to 1917. Oils were examined from about 2000 trees over a range of a latitude of about 250 miles[3]).

The production of camphor in Florida depends upon the planting of the trees in hedges and utilizing either the trimmings, consisting of leaves and small twigs, or by severely pruning the trees each year and distilling the resulting branches and leaves. Such trimming or pruning is done during one of the dormant periods, *i. e.*, during May to June or November to February.

It was found by repeated tests that with leaves and small twigs of the last growth, no cutting or grinding was needed, but the wood had to be cut into chips. Comparative tests with steam and direct heat distillations showed that better results were secured with the latter method. Hood calls crude camphor the mixture of camphor and oil, freed from the water. He pressed the camphor obtained by distillation, then separated the water from the oil and added this to the solid camphor. In order to ascertain the pure camphor in the crude, he stored the latter in well-stoppered bottles for at least two weeks and then separated the solid camphor from the oil by means of a centrifugal.

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[1]) Investigations of the Shô-Gyu and Yu-Ju Oils produced in Formosa. Monopoly Bureau, Government of Formosa. Taihoku 1914; *Report* April **1915**, 42. — [2]) *Journ. of Ind. and Engin. Chemistry* **9** (1917), 552. — [3]) Please consult our *Reports* October **1908**, 34; October **1915**, 9 and October **1916**, 10 for further notes on the cultivation of camphor trees in Florida.

As it was desirable to find out which parts of the camphor tree contained the largest proportion of camphor, so as to benefit from this knowledge in order to secure the most valuable material, distillations were made of the various parts of trees 8 to 12 years old. It resulted that the spring leaves contained more crude camphor than the summer leaves, but these were comparatively richer in pure camphor, most likely owing to the evaporation of the volatile constituents of the camphor oil (terpenes).

Furthermore, two 13-year-old trees were cut to the ground and the material sorted into leaves, twigs and wood of various ages, when it resulted that the young wood contains too little camphor to be taken into consideration for the production.

Experiments with trees of even age, some of which had grown in the shade, showed that shading has but little influence on the camphor content of the leaves, so that it does not matter in which direction the hedges are planted.

It has been repeatedly recommended to prune the trees strongly every year, but Hood succeeded in showing that by this method one gets a lot of wood with very little camphor in it and that even the camphor content of the leaves is thus reduced. The watery shoots are much poorer in camphor than normally grown branches or twigs. However, if the trees and hedges are only trimmed, a higher yield of camphor may be expected in the following period of vegetation.

Camphor trees are often planted in order to protect orange gardens against the wind or to replace orange trees that have died. Such trees are then manured sometimes, develop very well and contain much camphor. As a rule, quickly growing trees distinguish themselves by a thick foliage and considerable camphor content. This must be taken into consideration when cultivating camphor trees, in order to foster their growth as much as possible.

The soil likewise influences the camphor content. The greatest yield of camphor is supplied by trees growing on a heavy clayey soil and it decreases rapidly as the soil gets sandier and drier. It is true, however, that trees on extraordinarily dry sandy soil distinguish themselves by a very high camphor content, but such trees are considerably behindhand in growth.

Camphor contents of the various parts of Florida camphor trees: —

		crude camphor	pure camphor
spring leaves	from trees 8 to 12 years old	1.72 per cent.	1.31 per cent.
summer leaves	from trees 8 to 12 years old	1.46 „ „	1.14 „ „
spring twigs	from trees 8 to 12 years old	2.14 „ „	1.50 „ „
summer twigs	from trees 8 to 12 years old	1.22 „ „	0.89 „ „
leaves	of a tree 13 years old	1.12 and 1.17 p. c.	0.87 and 0.88 p. c.
this year's twigs	of a tree 13 years old	0.55 „ 0.59 „	0.48 „ 0.48 „
last year's twigs	of a tree 13 years old	0.36 „ 0.53 „	0.28 „ 0.39 „
branches, 1.9 to 3.8 cm. in diameter	of a tree 13 years old	0.53 „ 0.52 „	0.39 „ 0.38 „
„ 10.2 cm. in diameter	of a tree 13 years old	0.83 „ 0.53 „	0.58 „ 0.37 „
„ 17.8 cm. „ „	of a tree 13 years old	0.92 p. c.	0.60 p. c.
wood from the outer 4 annual rings of a branch 8 years old	of a tree 13 years old	1.26 and 1.87 p. c.	0.74 and 1.33 p. c.
wood from the inner 4 annual rings of a branch 8 years old	of a tree 13 years old	1.03 „ 1.21 „	0.53 „ 0.82 „
bark from the branches	of a tree 13 years old	0.56 p. c.	0.50 p. c.
„ „ „ trunk	of a tree 13 years old	0.11 „	0.07 „

On page 9 of our previous *Report*, we mentioned some cases of borneol having been offered as camphor. If the admission of such a substitute is somewhat comprehensible, this excuse cannot be valid for a sample of so-called camphor, recently submitted to our analytical laboratories. It had not the slightest relation with camphor, but was most likely an impure dipentene dihydrochloride, $C_{10}H_{16}2HCl$. We infer this from the strong chlorine reaction and from the m. p. of the substance between 45 and 49°. The sample being very little, a closer investigation was out of the question.

It is evident that such preparations are no substitutes at all for camphor, and it is unjustifiable to put them on the market, as much harm may be done by them. The only excuse would be, that the manufacturer was induced by the misleading and unfortunate designation of "artificial camphor" for pinene hydrochloride to produce something similar.

As to the determination of the camphor content in *Oleum camphoratum*, see page 92 of this *Report*.

Cardamom Oil. As it is known, two kinds of cardamoms are cultivated in southern India[1]), *i. e.* the Mysore cardamoms with round, smooth capsules, and the Malabar cardamoms with oblong rough capsules[2]). In the year 1914/1915, the exports amounted to 5850 tons to the value of $ 75269, half of which went to Great Britain and 15 per cent. to Germany. The prices were about 50 cents (American) per pound of ordinary dry cardamoms and $ 1 for bleached ones. Last year, $ 9.40 to $ 10.05 were paid per maund of 25 lbs. The cardamom plant is indigenous in western and southern India, where it is cultivated by natives as well as by Europeans. It has been impossible to determine the area under cultivation, but the increase in the prices during the last years has caused the plantations to be extended. The plant is frequently put between tea and rubber plants, without demanding special care or even artificial manuring. It bears already in the second year. The flowering time is in April or May and the fruits are collected in September or October. They are generally dried in the shade in the open air, but some growers dry them in hot air chambers and then bleach them with sulphur vapours.

Chamomile Oil. On the cultivation of chamomiles, see page 78 of this *Report*.

Oil of Wild Cherry bark. *Prunus virginiana* belongs to the plants containing amygdalin, the proportion being larger in the bark of the roots than in that of the branches and smallest in the bark of the trunk. C. Verne Nichols[3]) proved that this difference must be ascribed to the influence of sunlight. He examined the bark from the trunks of several trees and found that the parts from the side exposed to the sunshine contained 1/6 more amygdalin than those from the other side.

Oil of Chios Turpentine. As to the turpentine pistachio tree, we beg to refer to page 34 of this *Report*.

Cinnamon Oil, Ceylon. The decrease of cinnamon growing in Ceylon seems to be due in part to the introduction of the cultivation of rubber plants and to the

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., pages 284 and 287. — [2]) *Der neue Orient* **3** (1918), 40. — [3]) *Journ. Americ. pharm. Assoc.* **1917**, 540; *Pharm. Weekblad.* According to *Apotheker-Ztg.* **33** (1918), 87.

raised wages. The cinnamon plants offered no longer sufficient benefit and were cleared out therefore in many places[1]). Generally speaking, the extent of the cinnamon plantations has gone down continuously of late years. The exports had gone up gradually from 1904 to 1909. In the latter year, which signifies a turning-point, there was at first a standstill and then a retrograde movement. In 1913, the lowest stage of a decade had been reached. The increase of the exports in 1915[2]) was only fictitious, as a good deal of the 1914 crop was then shipped, which had had to be kept back owing to lack of tonnage. During the last years, the prices of cinnamon have sunk considerably, as the cheaper cassia bark from China found increased use as a substitute. 25 years ago, several thousands of acres were planted, in Ceylon, with a variety of cinnamon tree yielding in the beginning as much as 300 lbs. per acre. But this yield went down gradually to 100 lbs., in some cases even to 50 lbs.

The import of cinnamon into Ceylon and the cultivation of cinnamon are dealt with on page 83 of this *Report*.

Citronella Oil. According to a report issued by the Ceylon Chamber of Commerce[3]), 1 211 197 lbs. of oil of citronella were exported in 1917, as compared with 1 399 791 lbs. in 1916. The shipments to Great Britain, France and other countries decreased by 289 037 lbs., whereas the United States, Japan and Australia imported 100 443 lbs. more in 1917 than in the previous year. The foremost countries of destination were: —

	1917	1916
Great Britain	266 877 lbs.	432 161 lbs.
United States	745 026 „	681 921 „
Japan	38 221 „	25 414 „
France	11 303 „	80 940 „
Australia	121 758 „	97 227 „
other countries . . .	28 012 „	82 128 „

In the beginning of 1917, the price was from 75 to 77 cents per lb. It fell end of January to 62 to 65 cents and remained thus during February, March and April. Early in May, the prices rose to 65 and 68 cents, but then suddenly fell, the quotations up to end of June being 55 to 58 cents and end of July, 52 to 55 cents, which latter prices remained stationary up to the end of 1917. The averages for the years from 1914 to 1917 were as follows: 1914 = 89 cents, 1915 = 80 cents, 1916 = 87 cents, 1917 = 59 cents per lb.

The trade of the Dutch Indies with the United States increased considerably in these last years of war[4]), including the export of Java oil of citronella. It came up to 64 000 kg. in 1915, 196 000 kg. in 1916 and is estimated at 96 000 kg. in the first half of 1917. The total exports of citronella oil were 429 000 kg. in 1916 and 208 000 kg. in the first half of 1917.

Another periodical[5]) likewise reports an increase of the exports of citronella oil from Java. It is estimated at 400 000 kg. for 1916. The countries of destination were France, the United States, Japan and Great Britain. On a whole, 5500 bouw[6]) are planted

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[1]) *Der neue Orient* **1** (1917), 151. — [2]) Comp. *Report* October **1916**, 15. — [3]) *Perfum. Record* **9** (1918), 114. — [4]) *Handelsberichten (Den Haag)* **11** (1917), 503. — [5]) *De Ned. Olie, Vet en Zeep Industrie; Perfum. Record* **8** (1917), 54. — [6]) 1 bouw = 70.96 ares = abt. 1 3/4 acres.

with citronella grass. In the years 1912 and 1913, the exports from Java amounted to 169459 and 166070 lbs., equal to 76865 and 75327 kg., respectively[1]).

Clove Oil. According to an official communication[2]), on the islands of Zanzibar and Pemba there are approximately 60000 acres planted with clove trees, the number of which is estimated at 5500000. The yield varies considerably, a good crop resulting every three to five years. The average of the last years was 14000000 lbs. The largest crop was that of 1911/12, amounting to 28000000 lbs., 20000000 lbs. of which were supplied by Pemba. The smallest quantity was that of 1912/13, when only 4750000 lbs. were gathered, more than 3500000 lbs. of it in Pemba. The average for a plantation of about 3000 trees 60 years old, managed by a European, is 8 lbs. per tree, and there are 98 trees on each acre of land. The price during the last years fluctuated between Rupees 8.8.0 und 14.5.0 per frasilah of 35 lbs. The Government levies a tax of 25 per cent. on all exports of cloves.

The deliveries were as follows: —

	July 1st 1915 to June 30th 1916	July 1st 1916 to March 31th 1917
Zanzibar	4957399 lbs.	6715011 lbs.
Pemba	22929059 „	9644654 „
total:	27886458 lbs.	16359665 lbs.

For the remaining three month of the season 1916/17, the deliveries are estimated at from 1400000 to 1575000 lbs. The prices for 1 frasilah fluctuated during the season between 10.51 and 11.22 Rupees for Zanzibar cloves and 9.91 to 11.51 Rupees for Pemba cloves. The quotations have not been influenced by the war.

As to the export of cloves from Zanzibar, see p. 84 of this *Report.*

Coriander Oil. A sample of coriander grown in Cyprus and examined in the Imperial Institute, London[3]), gave the comparatively low oil yield of 0.48 per cent. other seeds of Moravian, Thuringian, Russian, and Hungarian origin giving 0.8 to 1 per cent. oil. Again, other samples are considerably poorer in oil, to wit, coriander from Morocco with 0.2 to 0.3 per cent. The oil from Cyprus coriander showed normal properties: — d_{15° 0.879, $\alpha_D + 12^\circ 20'$, n_{D20° 1.467, soluble in 1.9 vol. and more of 70 per cent. alcohol.

Oil of Crithmum maritimum. The French oil distinguishes itself in a remarkable way from the Italian product, although both are derived from the same plant[4]). M. Delépine and G. de Belsunce[5]) have attempted to ascertain the cause of this difference. They distilled plants from different districts of France, in the expectation of obtaining oils of dissimilar properties and composition. They found that really there were considerable differences in the properties of these oils. As, owing to the outbreak of the war, the investigations could not be completed, they published the preliminary results.

They first investigated the oil obtained from *Crithmum maritimum* grown near Batz (Loire-Inférieure) in the clefts of granite rocks on the coast. The soil in these clefts was extraordinarily poor in lime, the plants were little developped, reaching a hight of barely 20 cm., as compared with a normal hight of 50 cm. However, the content in ashes of

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[1]) Comp. *Report* October **1916**, 16. — [2]) Colonial report on the trade of Zanzibar for 1916; *Chemist and Druggist* **89** (1917), 1109. — [3]) *Bull. Imp. Inst.* **15** (1917), 301. — [4]) Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd ed., vol. III, pages 371 and 372. — [5]) *Bull. Soc. chim.* IV. **23** (1918), 24.

these plants was the same as that of plants collected on limestone rocks in the Charente-Inférieurs. The proportion of calcium in these ashes was very small, being only 0.26 per cent., as compared with 2 per cent. for the ashes of dry *Crithmum maritimum* stalks from the Charente-Inférieure. Notwithstanding, the oil content was the same for the plants from either source and their specific gravities showed but little difference, as may be seen in the following tables:—

Yield in oil from of *Crithmum maritimum* of various origin.

	Charente-Inférieure	Batz	Charente-Inférieure	Batz
date of gathering:	28. 8. 08	31. 8. 13	15. 9. 08	14. 9. 13
umbels . . . . . yield in oil from 1 ko. of fresh material	8.0 g.	8.0 g.	7.0 g.	7.6 g.
stalks with leaves . . . yield in oil from 1 ko. of fresh material	1.5 „	1.4 „	1.5 „	—
umbels . . . . . specific gravity	0.973	0.963	0.966	0.946
stalks with leaves . . . . . „ „	1.052	1.007	1.049	—
umbels . . . . . $[\alpha]_D$	6.1°	7.1°	6.2°	6.7°
stalks with leaves . . . . . „	7.2°	10.7°	6.7°	—[1]

Quite another result was arrived at with *Crithmum maritimum* grown on the limestone rocks of the Mediterranean coast, near Cap Ferrat (Alpes-Maritimes):—

date of gathering:	13. 10. 13	25. 10. 13
umbels . . . . . yield in oil	5.2 g.	5.6 g.
stalks with leaves . . . . „ „ „	1.8 „	2.2 „
umbels . . . . . specific gravity	0.891	0.886
stalks with leaves . . . . „ „	0.882	0.881
umbels . . . . . $[\alpha]_D$	4.2°	4.9°
stalks with leaves . . . . . „	4.7°	4.0°

In view of these results, material was gathered on 25th October 1913 in Cran-aux-Oeufs, in the neighbourhood of Cape Griz-Nez. The plants were rather small, not above 20 cm. in height, and had but few fruits. The result of the destillation was a follows:

	yield	spec. grav.	$[\alpha]_D$
umbels	8.9 g.	0.991	4.0°
stalks with leaves	3.3 „	1.087	4.14°
roots.	2.6 „	1.125	1.0°

Finally, once again plants from the Mediterranean coast (Fort-Carré near Antibes) were distilled. They had been gathered on 10th November 1913:—

	yield	spec. grav.	$[\alpha]_D$
umbels	3 g.	0.902	—
stalks with leaves	1.5 „	0.882	5.1°
roots.	0.5 „	0.895	—

A supply from Biarritz was almost useless. Stalks and leaves yielded an oil of a density of 0.974.

It has resulted, therefore, that the Mediterranean plants contain less oil than those from the Atlantic and Channel coasts. The oil from the former shows a smaller specific gravity, as it contains less apiole.

The following tables give details as to the content of the plants in dry substance, in ashes, and the proportion of calcium in the ashes:—

[1] The direction of the rotations is not indicated, as was the case too in previous French treatises on the same subject. The Italian oil, examined by Francesconi and Sernagiotto, showed $[\alpha]_D + 3.18°$.

Content in dry substance of *Crithmum maritimum* of various origin.

origin	dry substance	content in ashes of the plant dried at 105°	calcium content of the ashes
Charente-Inférieure	11.9 per cent.	17.6 per cent.	2.13 per cent.
Batz	— „ „	20.0 „ „	0.26 „ „
Cap Ferrat (I)	11.7 „ „	23.6 „ „	2.77 „ „
Cap Ferrat (II)	10.9 „ „	30.0 „ „	2.60 „ „
Cran-aux-Oeufs	11.9 „ „	25.0 „ „	1.84 „ „
Antibes	10.5 „ „	24.8 „ „	2.23 „ „
Biarritz	11.5 „ „	30.0 „ „	1.64 „ „

The saponification value and the ester value after acetylation were established for various oils. Both numbers were rather low. The authors further determined the content of the oils in dill apiole. The presence of this body can be proved in the fractions distilling above 160° (30 mm.) by converting it into the dibromide, melting at 110°. The dill apiole content of the different oils varies considerably, as is show in the following summary:—

Content of dill apiole in *Crithmum maritimum* of different origin.

origin	part of plant	d	content of apiole
Mediterranean	umbels	0.890	8 per cent.
	stalks with leaves	0.882	4 „ „
Batz	umbels	0.946	28 „ „
Cran-aux-Oeufs	umbels	0.991	40 „ „
	stalks with leaves	1.087	67 „ „
	roots	1.125	90 „ „
Biarritz	—	0.974	40 „ „

The content of dill apiole was judged by the quantities of high-boiling constituents.

All the oils examined contained thymol methyl ether, the presence of which is proved as follows: 1 cc. of oil, together with 2 cc. of hydrobromic acid (d 1.48) and 10 cc. of glacial acetic acid, is heated for 6 hours under a reflux condenser. Then, 20 cc. of water are added, the mixture is neutralized and afterwards extracted with ether. On evaporating the latter, crystalline thymol remains. The presence of the methyl alcohol, split off in this process, has been proved by the authors through transforming it into methyl iodide ($d_{18°}$ 2.23).

The authors have not been able, so far, to determine with certainty whether d-pinene occurs in the oil from the Mediterranean coast; the other oils contain this hydrocarbon.

Dipentene does not occur in the oil of *Crithmum maritimum*, Delépines former indication being due to a confusion with crithmene, the hydrocarbon which is characteristic for *Crithmum maritimum* oils. According to Francesconi and Sernagiotto, crithmene yields the following derivatives: α-nitrosochloride (m. p. 101 to 102°), β-nitrosochloride (m. p. 103 to 104°), nitrol piperinide (m. p. 138°), nitrol benzylamine (m. p. 103 to 104°), nitrosite (m. p. 89 to 90°), nitrosate (m. p. 104°), dihydrochloride (m. p. 52°). Delépine and de Belsunce have been able to detect neither the nitrosite nor the nitrosate; they have found the m. p. of 110 for the nitrosochloride and that of 148° for the nitrol piperidide.

β-phellandrene, present in the Italian variety, was not to be ascertained in the French oil of *Crithmum maritimum*.

The paraffine melting at 63° occurs in the French oils as well as in the Italian ones

Oil of Cryptomeria japonica. According to N. Yoshida[1]), for storing rice-beer, *sake*, in Japan, the casks are made of the wood of *Cryptomeria japonica*. The wood of this conifer contains an essential oil in which two sesquiterpenes, cadinene and suginene, as well as a sesquiterpene alcohol, cryptomeriol, have been found to be present. Yoshida has now found that the oil, especially the oxygenated fraction boiling between 270 and 286° acts as a moderate disinfectant. The casks made of fresh cryptomeria wood impart not only a special flavour to *sake*, but add also considerably to its keeping qualities.

Cumin Oil. A sample of cumin seeds originating from Cyprus, which contained about 3 per cent. of foreign seeds (apparently from a species of *Galium*), has been distilled in the London Imperial Institute[2]). The sample yielded 3.4 per cent. of a light-yellow oil with the following constants: — $d_{15°}$ 0.956, $\alpha_D + 1°30'$, $n_{D23°}$ 1.510, soluble in 1.1 vol. of 80 per cent. alcohol. The oil held 52 per cent. of aldehydes. A Cyprus oil which had been examined on an earlier occasion revealed the constants: — $d_{15°}$ 0.953, $\alpha_D + 1°39'$, n_D 1.514, soluble in 1.2 vol. 80 per cent. alcohol; aldehyde-content, 47 per cent. Both oils differ in their constants rather widely from the commercial oils, whose constants are: — $d_{15°}$ 0.900 to 0.930, $\alpha_D + 3°20'$ to $+8°$, $n_{D20°}$ 1.494 to 1.507, soluble in 3 to 10 vol. 80 per cent. alcohol and more; aldehyde-content (phenylhydrazine method) 35 to 42 per cent.

Nothing is stated as to how the Imperial Institute has estimated the aldehyde-content. As is generally known, neither the bisulphite nor the sulphite methods lead to satisfactory results with cumin oil. The determination by means of the phenylhydrazine method, however, gives results concordant within 1 or 2 per cent.[3]).

Oil of Darwinia grandiflora. From the leaves of *Darwinia grandiflora*, which they consider as genuine species, whereas Bentham treats it for a variety of *D. taxifolia*, R. T. Baker and H. G. Smith[4]) obtained a red volatile oil in a yield of 0.12 per cent. The material for distillation had been collected at the Hawkesbury River, N. S. W., in November 1917. The oil had the constants: — d 0.915, $\alpha_D + 23.1°$, n_D 1.4773, ester v. 100.4, scarcely soluble in 10 vols. 80 per cent. alcohol, and contained geranyl acetate, probably also geranyl butyrate. Of the oil, 30 per cent. boiled from 156 to 160°, it smelled of pinene and had the constants: — $d_{15°}$ 0.872, $\alpha_D + 41.6°$, n_D 1.4685. The fraction gives a nitrosochloride, m. p. 104°, and consists, according to Baker and Smith, of *d*-α-pinene.

Dill Oil, English. As we gather from a British periodical[5]), the 1917 English oil is remarkable for its particularly high rotation such as never been observed hitherto, as well as for its comparatively low specific gravity and low refractive index. The constants ranged as follows: — d 0.895 to 0.897, $\alpha_D + 83$ to $+88°$, n_D 1.481 to 1.483. For comparison, we cite here the constants of dill oil of English and other origin: — $d_{15°}$ 0.895 to 0.9245, $\alpha_D + 70$ to $+82°$, $n_{D20°}$ 1.484 to 1.490[6]).

The oil distilled in England, according to the same source, varies from season to season in physical characters and carvone content. The fruits do not ripen at the same time, and the herb is generally cut and packed in stacks for the fruit to ripen before they are separated for the distillation of the oil. The carvone content of the oil obtained from herb grown in hot summers is usually higher there that produced in cold or wet summers.

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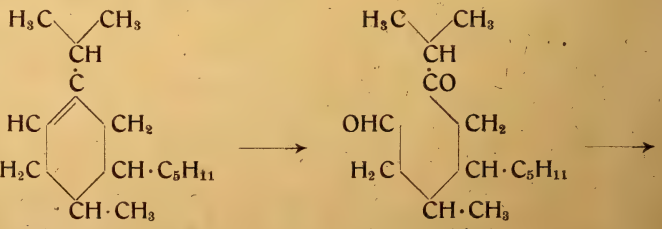
[1]) *Yakugakuzasshi* **1916**, No. 413; *Apotheker Ztg.* **32** (1917), 563. — [2]) *Bull. Imp. Inst.* **15** (1917), 302. — [3]) Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd edition, vol. III, p. 336. — [4]) *Proceed. Royal Soc. of N. S. W.* **50** (1917), 181; *Perfum. Record* 8 (1917), 305, 355. — [5]) *Perfum. Record* 8 (1917), 349. — [6]) Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd ed., vol. III, p. 399.

Elemi Oil. Some time ago, F. W. Semmler and Futung Liao[1]) investigated a sesquiterpene alcohol occurring in elemi oil which they termed "elemol". In the meantime, they have published[2]) new facts about elemol. For the purpose of elucidating its structure, the authors resorted to oxidation with aid of ozone which, however, in the case of the monocyclic sesquiterpene elemene (corresponding to elemol) did not furnish the result expected, possibly because owing to the presence of three double bonds in the molecule oxidation proceeds so rapidly that no decomposition products are obtainable. Hence it might be possible to obtain such bodies when starting from a partially hydrogenated elemene with only one double linking, *viz.*, tetrahydroelemene, and then to draw conclusions as to its structure. For this reason, the authors prepared at first pure tetrahydroelemol and, by dehydration, tetrahydroelemene.

Tetrahydroelemol was obtained from crude elemol by reduction with platinum and hydrogen and purified over its benzoate by treatment with pyridine and benzoyl chloride. The benzoate of the alcohol boils from 210 to 215° (13 mm.). On saponification it yielded saturated tetrahydroelemol, m. p. 35.5°, b. p. 138 to 142° (13 mm.). Tetrahydroelemol prepared from elemol (purified by means of its benzoate) by hydrogenation showed the same constants. With glacial acetic acid and sodium acetate, the alcohol formed tetrahydroelemyl acetate, b. p. 152 to 155° (12 mm.). On treatment with formic acid, tetrahydroelemol gave pure tetrahydroelemene which was subjected to the action of ozone under different conditions, *i. e.*, in glacial acetic acid or in acetic ester solution, with ozone in concentrations of 1 or 14 per cent. Decomposition of the ozonide was performed either by heating with glacial acetic acid or by reduction with zinc dust and the same solvent. In both cases, there resulted, in the main, the same reaction products, only in different proportions according to the method applied. Besides, a small amount of a monoketone, a ketonic aldehyde $C_{15}H_{28}O_2$ and a ketonic acid $C_{15}H_{28}O_3$ were obtained.

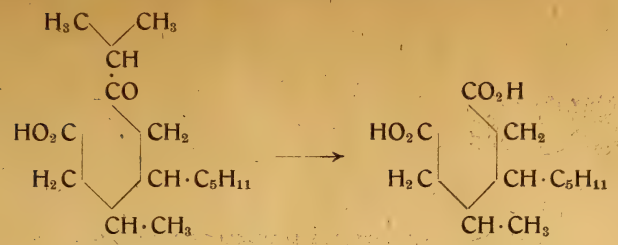
The neutral fractions, b. p. 120 to 140° (10 mm.), contained a monoketone, originating probably from the ketoacid, and mixed with ketoaldehyde. The principal fraction, b. p. 140 to 170° (10 mm.) contained the ketoaldehyde, giving with semicarbazide hydrochloride and sodium acetate in alcoholic solution a mixture of a mono- and a di-semicarbazone. On careful oxidation with cold potassium permanganate solution, the aldehyde yielded a ketonic acid $C_{15}H_{28}O_3$, b. p. 180 to 193° (10 mm.). A ketonic acid of the same formula occurred also in the acid parts of the ozonisation product.

In order to ascertain which alkyl group was linked to the CO grouping, Semmler caused alkaline bromine solution to act on the ketoacid, when a dicarboxylic acid, b. p. 180 to 205° (10 mm.) resulted, probably of the formula $C_{12}H_{22}O_4$, thus indicating loss of an *iso*propyl radicle by the oxidation process. The following formulæ would seem to apply to tetrahydroelemene and its degradation products, without, however, fixing the position of the side chain in the nucleus: —



Tetrahydroelemene. Ketonic aldehyde.

[1]) *Berichte* **49** (1916) 794; *Report* October **1916**, 20. — [2]) *Berichte* **50** (1917), 1286.



Ketonic acid. Dicarboxylic acid.

Since crude elemol and the resulting tetrahydroelemol showed constantly a higher specific gravity than the pure alcohol purified by means of its benzoate, the crude elemol fraction seems to contain a fair amount of impurities. Probably it is the case of a liquid isomeride of elemicin in elemi oil, or of another similar phenol ether containing perhaps a butenyl group instead of allyl, and the methoxyl groups in different position.

On a synthesis of elemicin, see page 138 of this *Report*.

Essential Oils, Sicilian and Calabrian.

Oil of Bergamot. A rather remarkable kind of bergamot oil was recently submitted to our laboratories for analysis. It originated from a small Dresden firm, chiefly engaged in the manufacture of "war" beverages and food substitutes and who sold the product with the guarantee that it contained 36 per cent. of esters. The buyer, however, having found out at once that he had been cheated, complained, but received no answer at all, a fact which does not speak in favour of the business methods of the firm in question. In consequence, the buyer was induced to ask for our opinion.

The sample was so small that it permitted only of determining a few of the constants, but this was quite sufficient to see that the oil had either been grossly adulterated or was an absolute failure of artificial substitute. The constants found were so abnormal that, to judge by them, nobody could possibly have guessed that the product was meant for oil of bergamot: $d_{15°}$ 0.9480, α_D — 16°, acid. v. 4.7, ester v. 136.3, whereas bergamot oil has a specific gravity of 0.881 to 0.886 and deviates from 8 to 22° to the right. The smell was likewise quite strange and pointed to the presence of an anthranilate, a body that does not occur in genuine bergamot oil. Owing to the small quantity available, it was impossible to ascertain whether linalyl acetate, the typical ester of bergamot oil, was present at all, but that much is certain, that the ester v. found and which would correspond to 47.7 per cent. (!) of linalyl acetate, is no criterion for the actual content of it, as the esters present were, totally or in part, of a different nature.

Oil of Lemon. Owing to the scarcity of lemon and orange oils, it seems that old stocks are now being thought of, but one generally makes the disappointing discovery that the oils have meanwhile become unfit for use in consequence of resinification. An astonishing number of such oils, partly offered to us, partly only submitted for inspection, have found their way to our laboratories. They all showed a high specific gravity, an increased residue on evaporation and a rotatory power, reduced in proportion with the rate of resinification. Some of the samples betrayed

their resinification by their viscosity. Naturally, the aroma of all these oils had suffered considerably, so that it was impossible to make them fit for use again even through rectification *in vacuo*.

As to adulterations, we would here mention an oil received from Hamburg. It showed normal specific gravity and rotation ($d_{15°}$ 0.8600; $\alpha_{D20°}$ + 60°), but the residue after evaporation was of a most suspicious nature. Quite apart from the fact that it was far too high (6.6 per cent.), it was not waxy like that of the genuine oil, but viscous and of an almost pure oily taste. It was to be deduced from this fact that the oil was either grossly adulterated or an artificial product.

Another artificial oil of lemon, originating from a small Leipzig firm, showed that the "art" had carried off the "artist". The only resemblance with lemon oil was its content of 5 per cent. citral, whereas the other properties were so absolutely different that it could in no way claim the name of "artificial lemon oil". The better half consisted of a resinous substance, the remainder of bodies boiling in the main between 220 and 260°. Terpenes showing the boiling point of limonene were not to be found in it. The strange composition expressed itself in the constants, especially in the lævorotation and the high residue after evaporation: $d_{15°}$ 0.9613, α_D — 14° 28′, residue after evaporation 58.4 per cent. Finally, we may say that the smell was nothing less than exquisite.

As per an official Italian communication, the stocks of oil of turpentine seem to be rather low in Italy, and as there are not enough buyers for lemon oil, in consequence of the reduced possibilities of export, the Government has taken steps in oder to decree the use of lemon oil instead of turpentine oil.

The Italian Ministry of Industry, Trade and Labour proclaims in the *"Gazzetta Ufficiale"*, No. 166, that the top price for lemon oil, meant as a solvent for varnish and enamel (?) for purposes of the State, has been fixed at Lire 8.50 per kg. The oil must have the following properties: 1. Pale colour and characteristic pure smell. 2. Specific gravity of 0.854 to 0.861 at 15°, at least 80 per cent. to distil over between 173 and 180°, the remainder up to 220°. 3. No more than 5 per cent. residue after evaporation on a water bath. 4. Purity and freshness to an extent that the oil may be considered appropriate for varnishes.

In an American periodical, there is a notice by F. Mc. Dermott[1]) on storing lemon oil. He points out that, as it is known, it easily deteriorates, even if kept in brown bottles, when in contact with the air, losing its fresh smell of lemons and taking a turpentine odour. In order to prevent this, it has been recommended to add 2 per cent. of olive oil or a certain proportion of alcohol and to store the oil in an carbonic acid atmosphere. Mc. Dermott is in favour of adding 10 per cent. of alcohol, as such a lemon oil keeps its odour unchanged for months. He therefore proposes to prescribe in the pharmacopœia the addition of 10 per cent. alcohol.

Oil of Orange. Our April *Report* 1915 contains, on page 22, some notes on the production and the properties of Jamaica orange oil, so that we need only say a few words here about an article recently published in an English periodical[2]) on the same subject. It is stated there that about 1200 fruits will produce 2½ lbs. of oil and that the adulteration with petroleum and cotton oil, formerly practised to a great extent,

[1]) *Americ. Perfumer; Pharm. Weekblad* **54** (1917), 721. — According to *Apotheker-Ztg.* **32** (1917), 379. — [2]) *Perfum. Record* **9** (1918), 57. — *Americ. Journ. Pharm.* **91** (1918), 187.

has almost ceased now. As to the quantities exported, the following tables are available: —

Exports of orange oil from Jamaica.

	1911		1912		1913		1914		1915		1916 [1])	
	boxes	dollars	boxes	dollars	boxes	dollars	boxes	dollars	boxes	dollars	boxes	dollars
Germany	—	—	88	6612	112	12663	80	7056	—	—	—	—
Belgium	—	—	—	—	—	—	19	302	—	—	—	—
France	—	—	—	—	—	—	14	224	—	—	—	—
Great Britain	160	7683	219	15719	244	17585	228	11585	195	9687	461	21162
United States [2])	33	1759	65	4396	466	35417	1033	57586	1276	55497	1953	119636
Canada	64	314	29	970	30	1214	66	2954	23	1040	10	543

It is used in Europe, but quite especially in the United States, in the manufacture of biscuits and sweets, but also for perfumes, soaps and flavouring essences.

The usual packing is in cases containing 2 coppers of 25 lbs. each.

Jamaica Orange oil is chiefly derived from sweet oranges.

As to the determination of the oil content in the *Citrus* fruit peels, see page 91 of this *Report*.

Eucalyptus Oil. A sample, sent us for analysis in March last, proved what incongruities occur with eucalyptus oil, especially in the retail trade. The bottle, holding about 30 grams, bore a label on which the eucalyptus oil, which it was supposed to contain, was praised up to the skies as a sort of panacea. The constants had been adapted to those of the Globulus oil, only the solubility was not up to the mark: $d_{15°}$ 0.9202, $\alpha_D + 1°17'$, soluble in 1 vol. and more of alcohol of 80 per cent., but of alcohol of 70 per cent. even 10 vols. were insufficient for a complete solution.

A closer investigation showed that the product had nothing whatever to do with eucalyptus oil, for it did not contain a single one of its characteristic constituents, but in the main bodies that are altogether alien to this group of oils. Apart from about 6 per cent. of ethyl alcohol, camphor was found to be an essential component of the stuff, amounting to about one third of the quantity. Borneol was likewise present, from which it may be concluded that one had here to deal with a camphor oil fraction containing camphor, to which apparently a mixture of waste terpenes had been added. The product was therefore an absolute failure and it only remained questionable whether the seller had been cheated or was trying to cheat. If the former was the case, he was still to be charged with carelessness, for he ought to have informed himself beforehand as to the properties of what he was going to put upon the market.

An English periodical [3]) publishes a notice with regard to the present state of the eucalyptus oil industry in New South Wales, part of which we beg to render here. The oil is obtained for three different purposes, *viz.*, pharmaceutical, metallurgical and technical for perfumery. Experts are of opinion that some eucalyptus oils may be used to a greater extent in future in order to prepare certain aromatics. The oil of *Eucalyptus Macarthuri* is specially mentioned, on account of the fact that it contains

[1]) Most likely the fiscal year ending on June 30th. — [2]) During the fiscal year ending on June 30th 1917, 69754 lbs. of oil to the value of $ 96553 were shipped from Kingston to the United States. — [3]) *Perfum. Record* 9 (1918), 94.

geraniol and geranylacetate. This species of eucalyptus grows quickly and can be propagated through seeds; the young branches do not only supply the largest quantities of oil, but also the oil richest in esters. Furthermore, *Eucalyptus citriodora* comes into consideration, the oil of which chiefly consists of citronellal and might be used as a cheap soap perfume. A third species, *Eucalyptus Staigeriana*, furnishes an oil which, owing to its citral content, is a cheap substitute for lemongrass oil.

The exports of eucalyptus oil from Australia to the United States and to Canada in the fiscal years[1]) of 1915[2]) and 1917 were as follows: —

	1915	1916	1917
Canada	206 £	180 £	1224 £
United States	1591 „	2434 „	4829 „

The oil is exported in tins of 4 gallons each; a box containing 2 such tins weighs 78 lbs.

Another notice in an Australian periodical (?) shows that considerable quantities of eucalyptus oils are used for metallurgical purposes, for it mentions that in working ores according to De Bavay's method about 300 tons are consumed annually. The quantity required for one ton of ore varies from $^1/_{20}$ to $^3/_4$ lb.

R. H. Crozier[3]) reports on the prospects of the development of the eucalyptus industry in British South Africa. Already some years ago, it is true, eucalyptus trees had been planted in the Union of South Africa, but they had not been exploited industrially so far. Crozier discusses the various kinds which, in his opinion, might be cultivated with success. Those eucalyptus trees, the oils of which are chiefly composed of pinene, such as *Eucalyptus lævopinea* and *E. dextropinea*, are of little importance. Oils of pharmaceutical interest are supplied by *Eucalyptus Globulus*, *E. polybractea* and *E. Smithii*, the last of which is quite specially fitted for being cultivated on account of its rapid growth. The eucalyptus species, the oils of which are used for metallurgical purposes and in the rubber industry, are *Eucalyptus amygdalina*, *E. dives* and *E. radiata*. Finally, the following species, mentioned before, are indicated: *Eucalyptus Macarthuri*, *E. citriodora* and *E. Staigeriana*.

Originally, *Eucalyptus amygdalina* had been cultivated in several places of the Union of South Africa, but at present its occurrence is limited to the elevated *"Randveldt"*. Small plantations are found in the Cape Colony and in Natal. Cool, damp mountainous regions, such as the eastern slopes of the Drakens Mountains, are specially suitable for their cultivation. In the warmer, rainy districts of South Africa, *E. citriodora* has been cultivated with success; it is very sensitive with regard to frost. Small plantations of it are found in Empangeni (Zululand), Durban, Maritzburg (Natal) and Kingwilliamstown (Cape Colony). *E. Globulus* is widely spread in the Union. Near Middelburg in Transvaal, there are small plantations of *E. Macarthuri* and of *E. Smithii*. *E. rostrata* prospers most in the interior, in the hottest and driest parts of the Union, provided that it is suitably watered.

It seems that Brasil also begins to take an interest in the cultivation of eucalyptus trees[4]). A decree of the Brasilian Government offers rewards to farmers, who in the next three years after the 6th March 1918 plant eucalyptus and other trees, from which essential oils can be obtained. The reward is 150 Reis for each tree at least 18 months old and of normal growth, if the number of trees is not less than 500. The decree

[1]) *Chemist and Druggist of Australasia*; *Perfum. Record* 8 (1917), 94. — [2]) The original says 1913, which is surely due to an error. — [3]) *South Africa Journal of Industries* of December 1917; *Perfum. Record* 9 (1918), 58. — [4]) *Perfum. Record* 9 (1918), 105.

grants land free of charge for the cultivation of eucalyptus trees, &c., and slips or seeds are supplied gratis by botanical gardens and other institutions under the control of the Board of Agriculture.

As it is known, the landscape in the Nilgiri Mountains has entirely changed its character, owing to the Australian eucalyptus and European trees that have been planted there. Eucalyptus leaves have been distilled already, but so far this industry has not attained to any importance. Puran Singh[1]) publishes some details regarding it. The oil of *Eucalyptus Globulus*, obtained in the Nilgiri Mountains, answers the requirements of the British Pharmacopœia, but its density is sometimes a little too low. Its properties are: d_{190} 0.9065 to 0.9155, α_D + 5° 28′ to + 9° 39′, n_D 1.463 to 1,466, acid v. 0.104 to 0.18, sap. v. 8.9 to 20, sap. v. after acetylation 17 to 21.68. It contains 60 per cent. of cineole (determined most likely according to the phosphoric acid method), is almost insoluble in alcohol of 70 per cent. but dissolves in less than 1 vol. of alcohol of 80 per cent. and is free from phellandrene. In addition to cineole, it contains pinene, sesquiterpenes and small quantities of free alcohols, but, in opposition to the Australian oil, neither eudesmol nor aldehydes.

The distillation of eucalyptus oil in the Nilgiri Mountains started about 30 years back, but it developed slowly and the annual production now is about 24000 lbs., the total quantity being sold in India itself. On a whole, 1900 acres are planted with eucalyptus trees. Through felling the trees, 5 tons of leaves are obtained per acre and year. It would be better to prune the trees, but this would be possible only with fresh plantations. As long as no fresh plantations can be started, from which leaves could be obtained by trimming the trees, there is but little possibility, according to Singh, of extending the eucalyptus oil industry.

The largest still in the Nilgiris holds about 800 lbs. of leaves, the distillation of which takes 6 hours. In order to obtain 1 lb. of oil, about 66 lbs. of dry or 114 lbs. of fresh leaves are required. The expense for fuel might be reduced to the extent of 25 per cent., if the distilled branches and twigs were dried and used for heating.

The mature green leaves, from trees planted in 1863, yielded 1.16 per cent. of oil, on an average, the dry ones about 2.28 per cent. Green leaves from trees ten years old contained 0.875 per cent., on an average, dry ones about 1.48 per cent. The leaves from shoots one year old yielded generally 0.83 per cent., if fresh, or 1.61 per cent., if dry. For another experiment the leaves of trees ten years old were dried in the shade, when the oil content was 1.39 per cent. for the material with 10 per cent. of moisture and 1.54 per cent. for absolutely dry material. Leaves dried in the sunshine and which still contained 9.7 per cent. of moisture, yielded 0.92 per cent. of oil, or 1 per cent., if calculated for absolutely dry material. It is evident, therefore, that a good amount of oil is lost on drying the leaves in the sunshine. Singh states that drying the leaves in the woods would mean a considerable economy as to transport.

An iron still will do for destillation, and if it was used with a helmet to hold back the impurities and heavy sesquiterpenes, it ought to be possible to obtain, without rectification, an oil that would come up to all requirements.

Oil of Eucalyptus Australiana. Already some time ago, we reported on the oil of this eucalyptus species described by R. T. Baker and H. G. Smith[2]). In another periodical,

[1]) *The Indian Forest Records* **5** (1917), No. 8; *Perfum. Record* **8** (1917), 326. See also *Handelsberichten (Den Haag)* **11** (1917), 472. — [2]) *Journ. and Proceed. Royal Soc., N. S. W.* **49** (1915), 514; *Journ. chem. Soc.* **110** (1916), I. 566.

we find more details concerning the work of the authors mentioned[1]). The leaves and terminal shoots of this species are particularly rich in oil, the average working yield being 2.5 per cent. in June and 3.4 per cent. in October. The oil distilling in the first hour is very rich in cineole and free from aldehyde-like bodies, and is set aside for pharmaceutical use. The product of the second hour is reserved for mineral separations and other technical purposes. The crude oil had the following characters:— $d_{15°}$ 0.9157, α_D + 2.8°, n_{D200} 1.4644, soluble in 1.2 vol. 70 per cent. alcohol, and contained 70 per cent. cineole. The "first hour" oil had a cineole content of 69.5 to 84 per cent., the "second hour" oil of 20 per cent., the characters of this oil being: — $d_{15°}$ 0.9291, α_D + 2.2°, n_D 1.4720. soluble in 1.1 vol. 70 per cent. alcohol. The "third hour" oil had similar properties and contained 26 per cent. cineole.

Oil of Eucalyptus Globulus. In a former *Report*[2]), we have drawn attention to the fact that the well-known *Eucalyptus Globulus* tree is unsuited for tropical climate. We find the same statement in an article on eucalypts in the Federated Malay States[3]), the climate of which does doubtlessly not agree with that eucalyptus species. The best success has been obtained there with *E. rostrata* (Red Gum) and *E. citriodora* (Lemon-scented Gum). Seedlings raised from eucalyptus thought to be *E. citriodora* have thrived particularly well and looked very healthy; its correct botanical identification is, however, only possible if they should flower. Probably, the humid atmosphere of the Federal Malay States is unsuited for most eucalypts.

Oil of Eucalyptus platypus. The latter species is amongst the comparatively few eucalypts about whose oil only little was hitherto known. Recently, J. C. Earl[4]) obtained from the fresh leaves of this species about 1 per cent. of oil with following characters: — d 0.9045, α_D + 9.1°, n_{D200} 1.4675, sap. v. 6, ester v. after acet. 24. It contained 59 per cent. cineole (by resorcinol absorption method), but neither aldehydes nor ketones. It gave 20 to 25 per cent. of pinene, 10 to 15 per cent. of phellandrene, 10 to 15 per cent. of aromadendrene and 5 per cent. of alcohols free and combined.

Nothing is to found in the abstract as to the method of identifying these constituents.

Oil of Eugenia Smithii. A. E. Dawkins[5]) obtained from the leaves of *Eugenia Smithii* (N. O. *Myrtaceæ*), in May, 0.44 per cent. of pale yellow, oil with a sweet penetrating odour; $d_{15°}$ 0.866, α_D + 35°, n_{D200} 1.4701. Another distillation in July gave a yield of 0.28 per cent. This oil had d 0.863, α_D + 34.6°, n_D 1.4675, and contained 80 to 90 per cent. of *d*-α-pinene, 4 per cent. of esters, and 3.7 per cent. of alcohols.

Geranium Oil. While engaged on experiments on utilizing the eucalypts in the Nilgiris, Puran Singh[6]) was struck by the profusion of wild geranium plants there, amongst them especially *Pelargonium graveolens,* L'Hérit. (*P. terebinthaceum,* Harv. et Sond.)[7]). One experimental distillation of the entire plant of geranium, whose leaves had began to turn yellow and flowers opened, gave 0.044 per cent. oil. Considering the season and the state of the plant collected, the yield was satisfactory, and the

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[1]) *Perfum. Record* 8 (1917), 50. — [2]) Comp. *Report* October **1913**, 54. — [3]) *Perfum. Record* 8 (1917), 161. — [4]) *Proceed. Royal Soc. Vict.; Chem. Abstr.* **1917**, II. 1715; *Perfum. Record* 8 (1917), 336. — [5]) *Proceed. Royal Soc. Vict.; Chem. Abstr.* **1917**, II. 2715; *Perfum. Record* 8 (1917), 358. — [6]) *The Indian Forests Record* 5 (1917), No. 8; *Perfum. Record* 8 (1917), 327. — *Americ. Journ. Pharm.* **90** (1918), 32. — [7]) It is now generally accepted that commercial geranium oil is distilled from *Pelargonium odoratissimum,* Willd., *P. capitatum,* Ait., and *P. roseum,* Willd. Ducellier, however, states *P. graveolens,* Ait. as sole species cultivated for distilling purposes. Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II, 614.

oil content of the Nilgiri geranium considered normal, but further experiments on this subject are necessary. The oil had the following properties: — $d_{16°}$ 0.888, α_D — 5°39', $n_{D18°}$ 1.460, sap. v. 96.25, ditto after acet. 226.08, total geraniol 74.79 per cent., combined geraniol 28.19 per cent., free geraniol 46.60 per cent., esters, calculated as geranyl tiglate, 40.12 per cent.

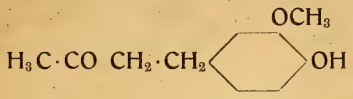
Ginger Oil. The pungent principle of the ginger rhizome, which does not occur in the oil, has been isolated already in 1882 by Thresh[1]) and was termed gingerol. He believed it to be a body $(C_5H_8O)_x$. Later on, Garnett and Grier[2]) found gingerol to possess phenolic characters and to lose its pungency when heated with alkalies. Brooks[3]) denied the existence of Garnett and Grier's gingerol, but erroneously, as is evident from recent publications by H. Nomura[4]) and by A. Lapworth, L. Kletz Pearson and F. A. Royle[5]). In both papers, the preparation of a pungent-tasting body of the formula $C_{11}H_{14}O_3$, termed "zingerone", from ginger rhizome is described. By degradation, the body revealed itself as *4*-hydroxy-*3*-methoxyphenylethyl methyl ketone (I). Whereas Nomura evidently believes zingerone to exist in the rhizome in the free state, Lapworth and his co-workers prove that it is a degradation product of another pungent component of the rhizome, gingerol.

Nomura prepared zingerone by extracting powdered ginger rhizome with ether in the cold and evaporating the extract to a syrupous consistency. The syrup was dissolved in a small quantity of ether and shaken with 2 per cent. sodium hydroxide. From the alkaline solution the pungent principle was deposited by means of carbon dioxide and extracted with ether. The ethereal solution was washed with sodium carbonate solution, then with water until the alkaline reaction disappeared, then dried over anhydrous sodium sulphate, and evaporated. The yield of residual oil was about 1 per cent. of the original ginger. It was distilled under 0.5 to 1 mm. pressure until the temperature of the oil bath reached 320°, after the previous distillation of volatile substance under 13 to 23 mm. pressure. The entire distillate dissolved in ether gave with sodium hydrogen sulphite a double compound from which zingerone could be regenerated, m. p. 40 to 41°. The benzoyl derivative melted at 126 to 127°, the acetyl derivative melted at 40 to 42° and boiled at 204 to 205° (14 mm.). Methyl-zingerone, obtained by shaking zingerone dissolved in sodium hydroxide with methyl sulphate showed after purification by means of its bisulphite compound the m.p. 55 to 56°; b.p. 186° (16 mm.); oxime, m.p. 93 to 93.5°. The methyl ether was identical with *3,4*-dimethoxybenzylacetone synthesised by A. Kaufmann and R. Radosević[6]). Ethylzingerone melts at 66°. Oxidation of methylzingerone with potassium permanganate in hot diluted sodium carbonate solution yielded veratric acid (II), m. p. 180 to 181°. Ethylzingerone, when oxidized with warm alkaline sodium hypochlorite solution, gave ethylvanillic acid, m. p. 195 to 196°. The same oxidation of methylzingerone gave rise to veratric acid and, probably, to *β-3,4*-dimethoxyphenylpropionic acid, m. p. 95 to 99°; when oxidized with sodium hypobromite, methylzingerone gave bromoform and *β-3,4*-dimethoxyphenyl propionic acid, m. p. 98 to 99° (III).

In order to synthesize zingerone, Nomura condensed vanillin (IV) with acetone to vanillalacetone or *4*-hydroxy-*3*-methoxystyryl methyl ketone (V)[7]) and reduced this compound by means of hydrogen in the presence of platinum black to *4*-hydroxy-

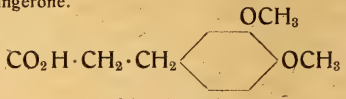
[1]) *Pharmaceutical Journ.* (III), **12** (1882), 721. — [2]) *Ibidem* **79** (1907), 118. — [3]) *Journ. Amer. chem. Soc.* **38** (1916), 430. Comp. also *Pharmaceutical Journ.* **98** (1917), 201. — [4]) *Journ. chem. Soc.* **111** (1917), 769. — [5]) *Ibidem* 777. — [6]) *Berl. Berichte* **49** (1916), 678. — [7]) Comp. L. Francesconi and G. Cusmano, *Gazz. chim. ital.* **38** (1908), II. 70; *Chem. Zentralbl.* **1908**, II. 1101.

3-methoxyphenylethyl methyl ketone, or zingerone (I). The synthetic product melted at 40 to 41° and showed no lowering of the melting point by mixing with the naturally occurring ketone. The benzoyl derivative and the oxime of the methyl ether melted, respectively, at the same temperature as the derivatives of the natural product, the melting points were not altered when mixing the synthetic and the natural products.

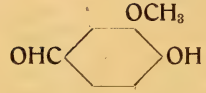


(I) Zingerone.

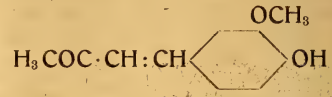
(II) Veratric acid.



(III) Dimethoxyphenylpropionic acid.



(IV) Vanillin.



(V) Vanillalacetone.

As mentioned above, Lapworth, Pearson and Royle regard zingerone as decomposition product of gingerol, the real pungent principle of ginger.

Lapworth and his collaborators isolated gingerol, the mother-substance of zingerone, from the alcoholic extract of African ginger by repeated treatment with alcohol of different strength, milk of lime, chloroform, and petroleum. In the pure state, gingerol is a liquid boiling even in a cathode-ray vacuum with slight decomposition. Its empirical formula is probably $C_{17}H_{26}O_4$ or $C_{18}H_{28}O_4$. To judge from its behaviour towards alkali, the presence of a phenolic hydroxyl group was probable. The alkaline solution formed with benzoyl chloride and similar bodies, or with chloroformic esters neutral, non-pungent, non-crystallizing compounds. Neither were solid derivatives obtained by the action of hydroxylamine, semicarbazide, phenylhydrazine, benzyl- or naphthylhydrazines. The sole derivative of gingerol obtained in crystalline form was the monomethyl ether, prepared by treatment of gingerol with methylalcoholic potash and methyl sulphate; m. p. 64°, $[\alpha]_{D20} + 27.3°$ (2 per cent. solution in chloroform). The methyl ether, methylgingerol, yields an oxime hydrate which showed Piloty's test for ketoximes (a yellowish-green coloration when treated with bromine water and hydrogen peroxide in presence of pyridine and ether). The authors did not succeed in proving the existence of a hydroxyl group by means of magnesium methyl iodide, although the substance reacts easily with acetyl chloride, thionyl chloride, and phosphorus chlorides. When oxidized with chromic acid, gingerol yields *n*-heptoic and (probably) *n*-hexoic acids. Oxidation of methylgingerol led to a mixture of fatty acids and veratric acid. When fused with potassium hydroxide gingerol gave, with strong carbonisation, rise to a small quantity of protocatechuic acid. Stenhouse and Groves[1]) had found the same acid in the product obtained by fusing crude ginger resins with potassium hydroxide.

By the action of heat and of hydrolytic agents on gingerol, a mixture of aliphatic aldehydes (mainly *n*-heptylaldehyde), and zingerone, is formed. From vacuum-distilled gingerol there was formed, by steam distillation, *n*-heptaldehyde, identified by its oxime (m. p. 53 to 55°) and by formation of *α*-hydroxy-*n*-octoic acid. In the non-volatile residue, zingerone is present, which may be separated by its bisulphite compound. The simplest way for preparing this ketone is to boil crude extracts of ginger with

[1]) *Journ. chem. Soc.* **31** (1877), 533.

baryta water as long as the distillate smells of œnanthol, acidify the residue, extract with ether, and shake with sodium hydrogen sulphite.

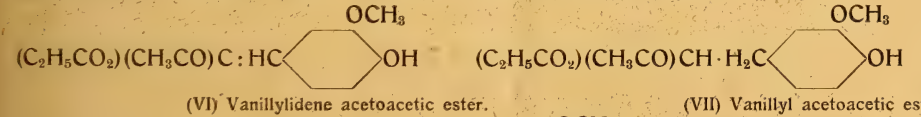
Methylgingerol, when treated with hydrolytic agents or when heated alone, gave rise to methylzingerone, besides aliphatic aldehydes.

Lapworth and his collaborators state zingerone to melt at 31 to 34°, Nomura 40 to 41°. It is but slightly volatile with steam and has a distinct, sweet odour reminiscent of salicylaldehyde and (less) of vanillin. Its phenylhydrazone melts at about 143°, its semicarbazone at about 133°, both compounds being difficult to purify. The ethylcarbonate melts at 45 to 47°. On methylation with methyl sulphate, methylzingerone is formed, m. p. 55.5 to 56.2° (Nomura: 55 to 56°). At any rate, both preparations of zingerone (of Lapworth and of Nomura) are identical, without regard to the difference in their melting points. By oxidizing methylzingerone with sodium hyperbromite, Lapworth and his collaborators obtained the same *β-3,4*-dimethoxyphenylpropionic acid as Nomura.

A synthesis of zingerone, methylzingerone, and some acids connected with these bodies has been described by A. Lapworth and F. H. Wykes[1]). They prepared from vanilline and acetoacetic ester vanillylidene acetoacetic ester (VI) according to the directions given by E. Knoevenagel and F. Albrecht[2]), dissolved the ester in dilute soda solution and reduced it to vanillyl acetoacetic ester by means of sodium amalgam. By saponifying the reaction product (filtered off from the mercury) with hot caustic soda they obtained vanillyl acetoacetic acid (VIII) which on heating *in vacuo* split off carbon dioxide with formation of a mixture of a phenol and an acid. On treatment of the former with chlorocarboxylic ester a body of the m. p. 47.5° resulted, which proved to be identical with the zingerone chlorocarboxylic ester mentioned before. When saponified, the ester yielded free zingerone, m. p. 36 to 37°.

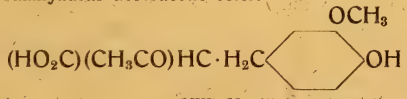
The synthesis of zingerone methyl ether was achieved by Lapworth and Wykes as follows: — veratric aldehyde (IX) and acetone were condensed to form *3,4*-dimethoxystyrylmethylketone (X) and the latter reduced, in alcoholic solution, by means of sodium amalgam to *3,4*-dimethoxyphenylethyl methyl ketone, or zingerone methyl ether. The ether thus produced was identical with the ether prepared from natural zingerone.

It is not impossible that zingerone is identical with "paradol" isolated by Thresh[3]) from grains of paradise. E. K. Nelson[4]), however, has found differences, yet he stopped his investigations on hearing of Lapworth's successful synthesis of zingerone. Whereas the pungent taste of gingerol disappears on boiling with alcoholic potash, it remains nearly unaffected in the case of paradol. From gingerol, Nelson obtained a solid methyl ether, m. p. 65 to 65.5°; paradol yielded the same ether.

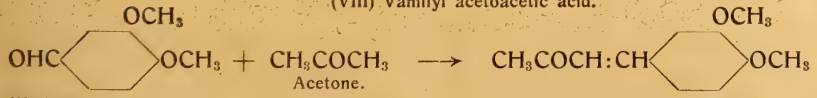


(VI) Vanillylidene acetoacetic ester.

(VII) Vanillyl acetoacetic ester.



(VIII) Vanillyl acetoacetic acid.



(IX) Veratric aldehyde. Acetone. (X) 3,4-Dimethoxystyryl methyl ketone.

[1]) *Journ. chem. Soc.* **111** (1917), 690. — [2]) *Berichte* **37** (1904), 4476. — [3]) *loc. cit.* — [4]) *Journ. Americ. chem. Soc.* **39** (1917), 1466.

Hyssop Oil. W. Himmelbaur[1]) found hesperidine as an abnormal crystalline secretion in *Mentha* plants attacked by fungi. O. Tunmann[2]) ascertained a similar increase of crystalline secretions in the hairier hyssop plants infected with fungi. However, the secretions were mixed crystals that did not contain any hesperidine, but the purified crystalline body did not dissolve at all or only in traces in water and the usual organic solvents, just like hesperidine. It was possible to obtain it in colourless prisms, melting at 275° from a solution in pyridine. Similar crystals occur in shepherd's purse. The body is being called hyssopine for the present but is most likely a derivative of flavone. Through melting it with potash, protocatechuic acid was determined with certainty. Hesperidine is absent in hyssop plants.

Lavender Oil. As per a notice in an English periodical[3]), the Grasse firm of Roure-Bertrand Fils negotiated some time ago with the French Government with the aim of taking over our Barrême distillery; however, the matter had to be renounced, as the French laws do not permit in such a case of a sequestered undertaking being transferred.

By the way, the French Government seems to have left this point of view, for in number 7 of July 1917 of *"La Parfumerie Moderne"*, there is an article on French lavender with a picture of our Barrême factory, at the bottom of which is to be read: *"Usine Schimmel désormais à MM. Gattefossé & Fils"*. In the article itself, it is stated too in a few words, that our distillery has been taken over by the firm of Gattefossé.

Some years ago already, the firm of Roure-Bertrand Fils founded a distillery at Laragne (Hautes-Alpes), in the centre of the lavender district, where an excellent oil of 50 to 55 per cent. of esters is distilled. As the prospects are held to be favourable, measures have been taken in order to increase the production and certain improvements of the steam distillation have been made, so as to ensure the manufacture of an excellent oil.

We see in this communication a proof of our working method being correct, for it was we who for the first time obtained in the South of France lavender oils with high ester percentages, by distilling the flowers rapidly with steam. According to the old method, the flowers were distilled with water, when part of the esters were saponified in the course of the slow distillation and the resulting oils were poor in esters, such as used to be sold formerly.

Regarding "lavandin" oil from British East Africa, see page 82.

Lemongrass Oil. We gather from an American Consular Report[4]) that British India (Cochin and Quilon) exported 30976 gallons to the value of $ 140480, in the fiscal year 1915/16 (ending in March), as compared with 27415 gallons to the value of $ 181034 in 1914/15.

According to another source[5]) the lemongrass oil trade was greatly handicapped by lack of tonnage, in 1916. In Madras, the freight to London via Suez was then quoted at £ 12 per ton. In January 1917, 680 dozen bottles of lemongrass oil were shipped to New York and 46 dozen bottles to Marseilles. The total export from July 1st 1916 to 31st January 1917 amounted to 11407 dozen bottles, of which 1671 dozens went to Great Britain, 7064 dozens to France, 2685 dozens to America, and 7 dozens each to Japan and Bombay.

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[1]) *Zeitschr. f. d. landwirtsch. Versuchswesen in Österreich* **1914**, N° 3/4; *Report* April **1915**, 32. — [2]) *Pharm. Post* **50** (1917), 773; *Chem. Zentralbl.* **1918**, I. 29. — [3]) *Perfum. Record* **9** (1918), 78. — [4]) *Perfum. Record* **7** (1916), 396. — [5]) The Oil and Colour Trades Journal; *Handelsberichten (Den Haag)* **11** (1917), **447**.

K. Kafuku's investigations[1]), carried out some time ago, pointed to the probability of the aliphatic terpene myrcene being present in Formosa lemongrass oil. He now thinks[2]) he has definitely proved the presence of this body in the following way: He reduced the terpene with sodium and alcohol, when a substance resulted showing the properties of dihydromyrcene and which afforded a tetrabromide melting between 87 and 88°. A further hydrogenation with hydrogen and platinum led to 2.6-dimethyloctane. On oxidation with alkaline potash permanganate, succinic and oxalic acids were formed. The oil contains an aldehyde which is not identical with citral and which it has not been possible, so far, to identify.

Lime Oil. The cultivation of lime in the West Indies has been repeatedly discussed in our *Reports*[3]). It seems that it is increasing continually, as lime juice, for the manufacture of which the fruits are chiefly used, is very popular in England and in the United States. An official report about the Leewards Islands[4]) says that the plantations of limes extend there over 970 acres. On the St. Lucia Island, the lime juice and oil industry is likewise progressing. In Montserrat, the plantations have to suffer much from illnesses and from insects, although the conditions have improved somewhat owing to the heavy rains in 1915. In the same year, the Dominica crop amounted to 390458 barrels. There, the storms of August 1915 caused severe damage, uprooting 10000 to 12000 trees, which means a loss of 14000 to 15000 barrels of fruits. The exports of oil of limes in 1915 were as follows:

essential oil of limes = 4108 gallons to the value of £ 9985,
otto of limes . . . = 974 „ „ „ „ „ „ 2484[5]).

In the preceding year, the value of the export was £ 12626 higher.

The periodical *Tropenpflanzer*[6]) contains a communication on lemon growing in Dominica. This would be something quite new, for so far only limes but no lemons have been cultivated there. We take it, in consequence, that some confusion occurred in translating. The editors of said periodical, whom we approached on the subject, declared, however, by letter that only lemons had been mentioned in the original, which it was impossible to trace. Nevertheless, we maintain our doubt, all the more as the figures mentioned in the *Tropenpflanzer* tally almost entirely with those given for limes in the Blue Book of the Leewards Islands for 1916/17[7]). According to it, in 1916, the exports of essential oil of limes came up to £ 16803, those of otto of limes, to £ 2435. These denominations refer most likely to hand-pressed and distilled oils.

In Onderneeming (Demerara, British Guiana), the Government founded an institution with the task to examine the question of vitality of the lime fruit industry. We have now before us the report on the six first months of work[8]). The quality of the fruits supplied by the various growers was not always satisfactory. Sometimes, they were absolutely unripe or showed damage done by insects, this latter fact being a proof of the trees having been neglected. The juice obtained was very good, but the yield in oil rather low, owing most likely to lack of experience. In any case, the average results are satisfactory, and the prospects favourable, for the lime fruit industry in the neighbourhood.

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[1]) Comp. *Report* October **1917**, 30. — [2]) Kogyo-Kwagaku-Zasshi (*J. Chem. Ind. Tokyo*) **20** (1917), 825; *Journ. Soc. Chem. Industry* **37** (1918), 74 A. — [3]) Comp. *e. g. Report* October **1915**, 18. — [4]) *Perfum. Record* **8** (1917), 109. — [5]) These names are new to us, as one generally differentiates between hand-pressed oil of limette or lime oil and distilled oil of limette or distilled lime oil. — [6]) *Tropenpflanzer* **21** (1918), 64. — [7]) *Perfum. Record* **9** (1918), 69. — [8]) *Perfum. Record* **8** (1917), 109.

The lime fruit tree has been planted too in some parts of British West Africa and has got acclimatized in several cases. In Nigeria, it grows in numbers in certain districts[1]), so that the fruits might be used there for manufacturing purposes. The Imperial Institute examined an oil from there which had been distilled from the whole fruit, the yield being from 0.13 to 0.21 per cent. It smelled agreeably of lemons and showed the following constants: $d_{15°}$ 0.8946, $\alpha_{D20°} + 34°4'$, $n_{D21°}$ 1.4815.

Lovage Oil. As to the cultivation of lovage, see page 78 of this *Report*.

Marjoram Oil. As marjoram oils obtained in Germany may be considered comparitive rarities, we here beg to mention one, distilled by us last year from the fresh plant. The yield was very scanty, being only 0.05 per cent., whereas it is generally from 0.3 to 0.4 per cent. The properties were: $d_{15°}$ 0.9003, $\alpha_D + 23°4'$, $n_{D20°}$ 1.47112, acid value 0.9, ester v. 31.7, soluble in 0.8 vol. and more of alcohol 80 per cent.

Mastic Oil. H. Banning[2]) reports on the economical importance of the pistachio trees in Turkey. Among the numerous kinds, only three are of special interest, *i. e.* the true pistachio tree (*Pistacia vera*, L.), the mastic pistachio tree (*P. lentiscus*, L.) and *P. terebinthus*, L. (*Anacardiaceæ*). Only the latter two come into consideration for us. The mastic pistachio tree is sensitive towards severe winters, which may destroy whole plantations of it, such as the one of 1849/50 did on the island of Chios. The variety cultivated there has been designated by botanists as *P. lentiscus var. Chia* and distinguishes itself from the wild growing species by its tree-like character.

In order to obtain quantities of gum mastic, holes were bored formerly into the trees with the aid of sharp little irons. Nowadays, only 6 or 7 slight incisions are made into the bark of the trunk and the principal branches. With regard to the direction of the resin ducts, cross-like incisions are more rational than the customary longitudinal ones; a kind of circular incisions are also practised. From these the juice slowly exudes and either hardens in tears upon the bark, or, if the flow is too strong, drops on the ground, where it is received on cloths, on flat stones, or on the soil, which has previously been swept and covered with a thin layer of ashes. The resin does not adhere to the soil but hardens and is collected after 2 to 3 weeks by women or children with the hands. One person can seldom gather more than 1 to 1½ oka daily[3]). The drops are taken off the trees with tongs or knives and collected into lined baskets. Rain is detrimental to the crop. The first tapping takes place between the 15th and 20th July (old style), and two more follow up to September. In former centuries, the periods for the crops were fixed by law for reasons of political economy. The first tapping was not allowed before 27th August (old style) and lasted eight days. The trees were then tapped again on about September 25th, when the crop lasted eight days once more. After that time, it was allowed to collect the mastic every Monday and Tuesday up to 19th November, after which day further collecting was forbidden. Formerly, the crop was taken to the Government's quarters in town, accompanied by a music band. All the officials present received a certain share for their trouble in taking over the crop, for they had originally had to fetch the mastic from the villages after it was sieved.

A mastic tree yields 3 to 4 okas annually, sometimes even more. The productivity of the trees decreases with age. The yearly crop was 550000 to 600000 kg., 15 to

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[1]) *Bull. Imp. Inst.* **15** (1917), 177. — [2]) *Archiv f. Wirtschaftsforschung im Orient* **1917**, number 3/4. — [3]) 1 oka = 1 to 1¼ kg.

20 years ago, drops and blocks taken together, when the former constituted about two thirds of the total. Chios exported 219440 kg. in 1906, 190020 kg. in 1907, 219230 in 1908 and 238290 kg. in 1909. During the 5 or 6 last years, the crops amounted to little more than 350000 kg. and have decreased since then continuously, whereas the prices are rising. The 1913 crop, estimated at about 200000 to 225000 kg. only, was specially small. In 1914, the crop left again much to be desired, but there was too a certain slackness in the exports, as Chios began to suffer under the difficulties of transport caused by the war. In consequence, there was no mastic to be had in Constantinople, in 1915, when the demand of the Central Powers was very keen.

There are two kinds of mastic in commerce, the drops or grains *(mastiche in granis)* and blocks. The best qualities are transparent tears or oblong cilindrical pieces of only 0.5 to 2 cm. in diameter and which look slightly greenish in a fresh state. This greenish hue disappears very soon, so that the article is then colourless. Inferior qualities are yellowish or brownish, form one mass, and contain more or less admixtures of parts of the plant, soil and sand.

Mastic played an important part as a medicine in former centuries, and the physicians of the Middle Ages praised its healing power. It was chiefly used for chewing. Formerly, the absolutely pure, so-called harem quality was not on the market at all, for the Customs officers took it all to send it to the Turkish court, the average quantity being about 60000 lbs.

P. terebinthus, L., also called turpentine tree, occurs already near Bozen and in the South of France, but there it neither furnishes resin nor edible fruits. Near Constantinople, the tree attains a considerable hight.

In addition to the turpentine pine *(Pinus taeda)*, *Pistacia terebinthus* comes into consideration for the production of turpentine in Chios. The method is the same as with other trees. In Turkey, holes are made into the trunk, instead of incisions only, and the resin is collected on flat dishes put underneath.

E. Sernagiotto and N. Vita[1]) obtained about 0.5 per cent. of a volatile oil containing a terpene-like body, on distilling the fatty oil of mastic tree seeds with steam. The properties of this volatile oil are: $d_{15°}$ 0.8654, α_D 0, b. p. 165°, bromine value 285.4.

Oil of Meum athamanthicum. We had in this year, for the first time, the opportunity of distilling the oil from the *fresh* roots of *Meum athamanthicum* Jacqu. (N. O. *Umbelliferæ*), which is of interest since hardly anything is known about this oil. Thirty years ago[2]) we prepared the oil from the *dry* roots of the same herb and succeeded in obtaining 0.67 per cent. of a dark yellow oil, viscid or even solid at ordinary temperature; $d_{21°}$ 0.999. The new oil, from the the fresh roots (yield, 0.48 per cent.) behaved decidedly different; it was limpid, orange-yellow, and had the constants: — $d_{15°}$ 0.9807; α_D — 1°55′; $n_{D20°}$ 1.51898; acid v. 10.3; ester v. 151.2. The oil was insufficiently soluble in 10 vols. 80 per cent. alcohol, but easily soluble in 0.3 and more vol. 90 per cent. alcohol; the diluted solution, however, was not clear, but showed very slight opalescence. The roots had been collected in the Saxon *"Erzgebirge"*, in the beginning of June, 1918.

Mustard Oil. Owing to the increased demand for fatty mustard seed oil, the area under cultivation with mustard in Russia has been extended by 25 per cent. Whereas 39588 desjatines were used, in 1916, for growing mustard, it was about 9000 des-

[1]) *Annali chim. applicata* 4 (1915), 92; *Journ. Soc. Chem. Industry* 34 (1915), 1061. — [2]) *Bericht* April 1889, 43.

jatines larger in 1917. As the average crop is 50 poods per desjatine, the total would come up to 44700 poods in 1917, as compared with 35700 in the previous year. There are no exact export figures available; however, as one may take it that 40 per cent. of the exports of vegetable oils are derived from mustard, this would mean about 252 tons for 1916[1]).

Oil of Ocimum viride. Some years back, the Imperial Institute sent us a sample of the oil of the labiate *Ocimum viride*, Willd., containing about 52 per cent. of thymol[2]). Said Institute[3]) thinks that this oil may come into consideration for the manufacture of thymol on a large scale. The plant is indigenous in tropical West Africa and has been introduced into India, Cyprus and the West Indies. It is frequently called mosquito plant, although it is in no way efficacious against gnats[4]). Leaves of *Ocimum viride* from Nigeria and Sierra Leone have been examined by the Imperial Institute. They yielded 0.35 to 1.2 per cent. of volatile oil, the thymol content of which fluctuated between 32 and 65 per cent. In order to find out whether and how the cultivation of *Ocimum viride* would pay, if carried out for the manufacture of thymol, experiments were made of growing the plant in Cyprus, British East Africa and on the Seychelles. The results on the Seychelles were favourable. Plants two months old were put out there in good garden soil, when after 6 months they had reached a hight of 6 feet. Two trial distillations were made. In the first instance, plants 4 months old were distilled during the dry season in October 1916. The yield from the leaves was 0.5 per cent. A second cut was made during the rain period, when the plants were 8 months old. Only the upper parts of the stalks with the flowers were then used. The yield came to 0.45 per cent., calculated for fresh material. Presumably, 5 to 6 cuts may be possible annually.

The oils had the following properties: —

	oil of *Ocimum viride* from plants from the Seychelles		oil from Sierra Leone
	4 months old	8 months old	
yield	0.45 per cent.	0.5 per cent.	—
$d_{15°}$	0.942	0.924	0.911
α_D	+ 1° 5′	+ 0.6°	+ 1° 30′
phenole content	62 per cent.	52 per cent.	to 65 per cent.
soluble in	3.1 vols. of alcohol of 70°	20 or less vols. of alcohol of 70°	—
	1.4 vol. of alcohol of 80°.		

Oregon Balsam Oil. Some years ago G. B. Frankforter and F. C. Frary[5]) isolated from the crude oleoresin of the Western fir a terpene which they regarded as different from pinene and termed "firpene". This terpene war said to differ from pinene especially in not giving a nitrosochloride. Now, A. W. Schorger[6]) has found when examining the oleoresins from the heartwood as well as the living wood of the Douglas fir (*Pseudotsuga taxifolia*, Britt.; *P. Douglasii*, Carr.)[7]) firpene to be highly active *l*-α-pinene.

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[1]) Foreign report of the *Kriegsausschuss für Öle und Fette; Seifenfabrikant* **38** (1918), 179. — [2]) *Report* October **1911**, 63. — [3]) *Bull. Imp. Inst.* **15** (1917), 322. — [4]) Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd ed., vol. III., page 621. — [5]) *Journ. Amer. chem. Soc.* **28** (1906), 1461; *Report* April **1907**, 130. — [6]) *Journ. Amer. chem. Soc.; Perfum. Record* **8** (1917), 194. — [7]) It appears from Schorger's paper that "Western fir" and "Douglas fir" are identical trees.

The gum had been collected by a forest ranger personally and was positively unadulterated. A wind-shake in a tree produces a pocket which in time fills with oleoresin. If such a pocket is struck by boring, the oleoresin soon flows out; frequently, from one to three gallons are obtained from a single boring. The oleoresin from the heartwood contains about 30 per cent. of volatile oil. Two oils, after rectification with steam in presence of caustic soda, had the properties: — $d_{20°}$ 0.8615 and 0.8627, $[\alpha]_{D20°}$ — 47.38 and — 46.36°, $n_{D20°}$ 1.4688 and 1.4690. About 60 per cent. of the oil boiled between 156 and 157°, and consisted of *l*-α-pinene, whose constants were nearly identical with those of the firpene of Frankforter and Frary: —

	Firpene	*l*-α-Pinene from Oregon balsam oil
B. p. . . .	153 to 153.5°	156 to 157°
$d_{20°}$ . . .	0.8598	0.8590
$[\alpha]_D$ . . .	— 47.2°	— 47.52°
$n_{D20°}$ . . .	1.47299	1.4670

It was identified by transformation into *l*-α-pinonic acid, m. p. 68°; $[\alpha]_{D20°}$ — 89.18° (0.03642 g. in 1 ccm.); m. p. of the semicarbazone 107°. On account of the high optical rotation the *l*-α-pinene did not yield a nitrosochloride.

Neither camphene nor β-pinene were detected in the oil.

5 per cent. of the oil boiling between 168 and 178° consisted of *l*-limonene; m. p. of the dihydrochloride 49 to 50°.

The highest-boiling parts of the oil were free from methoxylated bodies, but *l*-α-terpineol (nitrosochloride, m. p. 116°; nitrolpiperidine, m. p. 152°) was present.

The oleoresin obtained from the living wood by tapping yielded 22.7 per cent. of oil with $d_{19°}$ 0.8594, $[\alpha]_{D19°}$ — 22.36°. It contained about 17 p. c. *l*-α-pinene (nitrosochloride, m. p. 103°; nitrolpiperidine, m. p. 132,5°). Camphene was not detected, but about 46 per cent. of *l*-β-pinene, yielding on oxidation nopinic acid, m. p. 125°.

Possibly, this oil also contains limonene.

Origanum Oil. According to a communication of the Imperial Institute[1]), Cyprus exported in 1915 34 cwts. origanum oil valueing 1.046 £ to Great Britain. The ordinary Cyprus oil is stated to originate from *Origanum dubium,* Boiss. (see below). Later on, a further species of *Origanum*[2]) has been described, *O. Bevani,* Holmes which is also distilled in Cyprus. The Imperial Institute received of this species, some time ago, a sample of 49 lbs. of dry flowering herb, without the roots. The plant had a particular, thyme-like odour and gave 1.9 per cent. volatile oil with the characters: — $d_{15°}$ 0.951; α_D + 0° 24′; $n_{D23°}$ 1.51; soluble in 2.7 vol. 70 per cent. alcohol; phenols 75 per cent. Normal Cyprus oils have the constants: — $d_{15°}$ 0.958 to 0.966; $\alpha_D \pm 0$; $n_{D23°}$ 1.51; soluble in 1.4 to 2.8 vol. 70 per cent. alcohol; phenol content 75 to 82,5 per cent. The phenols of the oil of *Origanum Bevani* consist of a mixture of about 41 parts of carvacrol and 34 parts of thymol, ordinary Cyprus oil is said to contain merely thymol. For this reason, the distillation of *O. Bevani* is not to be recommended, and the prospects therefor do not seem to be great, since this species occurs only scarcely in Cyprus.

We wish to add to above communication that it is rather doubtful whether Cyprus origanum oil contains merely thymol. According to the statements of the Chemist to the Cyprus Government, Francis, the oil, it is true, consists principally of a mixture of thymol, thymene and cymene; on the other hand, the phenols of Cyprus oil investi-

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[1]) *Bull. Imp. Inst.* **15** (1917), 305. — [2]) E. M. Holmes, *Perfum. Record* **6** (1915), 19; *Report* October **1915**, 29.

gated formerly by the Imperial Institute and by us were identified as carvacrol. S. Pickles[1]) is of opinion that the analyses of Francis and Saracomenos, who found more there 80 per cent. thymol in the oil, were based merely on the results of fractionation, without chemical identification of the constituents. Besides, Francis seems to have believed his oil to be thyme oil, the carvacrol, in consequence, by mistake, to be thymol.

Furthermore, we have doubts whether the common Cyprus oil is actually a product of *Origanum dubium*. Holmboe believes the mother-plant to be *O. dubium*, a subspecies of *O. Maru*, L., whereas Holmes claims *O. majoranoides*, Willd., a variety of *O. Maru*, for that character. Besides, it must be remembered that the systematology of the *Origanum* species is difficult and not yet sufficiently clear[2]).

Palm Kernel Oil, essential. Commercial palm oil is prepared in the tropics from the fruit of *Elœis guineensis*, Jacq. (N. O. *Palmæ*), whereas palm kernels are worked principally in Europe for their fatty oil. Equally to cocoanut oil, palm kernel oil must, for edible purposes, be freed from ill-smelling constituents by steam distillation. In this process, an essential oil is obtained which, according to A. H. Salway[3]), shows the following figures: — $d^{20°}_{20°}$ 0.842; acid v. 30; ester v. 15. Shaking with 1 per cent. sodium hydroxide solution removed 12.2 per cent. of free fatty acids from the oil. The remaining oil boiled, under 90 mm. pressure, between 135 to 165° and was collected in three fractions, each of which reacted with sodium hydrogen sulphite. The oil regenerated from the double compound solidified in the cold and showed the following properties agreeing with those of methyl nonyl ketone: — m. p. 13°; b. p. 220 to 230°; $d^{20°}_{20°}$ 0.828. Its semicarbazone melted at 122 to 124°, its oxime at 44 to 46°. The amount of volatile neutral oil contained in palm kernel oil was 0.11 per cent.

In connection herewith we report in the following on an essential oil which we received from a large soap works. It was then prepared by distilling 80 kilos palm kernel oil with steam and extracting the distillate with toluene. Some of the solvent was still present in the oil.

The oil distilled, under 5 mm., between 45 and 125° (108 g.) and was freed from fatty acids by shaking with potassium carbonate solution. The neutral essential oil showed on boiling the following behaviour: —

fraction I 4 g., b. p. 40 to 65° (7 mm.)
fraction II 58 g., b. p. 65 to 100° (7 mm.)

The latter fraction smelled of rue and had the constants: — $d_{15°}$ 0.8325; $\alpha_D \pm 0$; $n_{D20°}$ 1.42785; sol. p. + 2°. On shaking this fraction with acid sulphite solution 90 g. of a bisulphite compound were obtained which after decomposing with sodium carbonate and steam distilling gave 45 g. of rue-like smelling ketones. They distilled from 180 to 232° (740 mm.) and could be separated, by repeated fractionation, into a part boiling between 180 and 230° and one distilling without alteration from 230 to 232°. The latter, 18 g., proved to be pure methyl nonyl ketone. M. p. 12 to 13°; $d_{15°}$ 0.8299; $\alpha_D \pm 0$; $n_{D20°}$ 1.43075; m. p. of the semicarbazone 121°. The semicarbazone prepared from rue oil showed the same melting point. On oxidation with bromine and caustic potash, the ketone yielded n-caprinic acid, m. p. of the raw product 27°; the amide, prepared by means of the ammonium salt (white leaflets from light petroleum) had the m. p. 97 to 98°.

From the lower boiling ketone fraction, no semicarbazone of exact m. p. could be isolated. Probably it is a question of methyl amyl and methyl heptyl ketones.

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[1]) *Journ. chem. Soc.* **93** (1908), 862; *Report* November **1908**, 90. — [2]) Compare Gildemeister and Hoffmann, *Die ätherischen Öle* 2nd ed., vol. III, 59. See also *Report* October **1913**, 77. — [3]) *Journ. chem. Soc.* **111** (1917), 407.

Japanese Pepper Oil. Several papers dealing with the oil of the fruits of so-called Japanese pepper *(Xanthoxylum piperitum*, D. C., N. O. *Rutaceæ)* have been published. Some time ago, Schimmel & Co.[1]) believed citral to be a constituent of the oil. Recently, Y. Asahina and U. Konno[2]) have found 15 per cent. citronellal to be present in the oil, nothing, however, appearing in the abstract available as to the method of its identification. The oil was colourless, mobile and smelled of citronella oil. $d_{4^\circ}^{19^\circ}$ 0.8511; $[\alpha]_{D20^\circ} + 45.45^\circ$; acid v. 1.35; ester v. of the aldehyde-free oil 18.78. The non-aldehydes contained principally terpenes and yielded with nitrous acid a nitrite, m. p. 203 to 204°; $[\alpha]_D + 159.9^\circ$. On oxidation with potassium permanganate and subsequent treatment with acids it yielded a substance smelling of cuminaldehyde, the semicarbazone of which showed a m. p. of 203 to 204°, agreeing with that of tetrahydrocuminaldehyde prepared from β-phellandrene in the like manner. However, β-phellandrene isolated by Wallach from the oil of *Phellandrium aquaticum* is dextrorotatory and yields a lævorotatory nitrite. Hence it is probable that xanthoxylum oil contains lævorotatory β-phellandrene, whose rotation appears to be inversed owing to the presence of a dextrorotatory terpene.

Peppermint Oil, Japanese. In addition to the numerous components of Japanese peppermint oil, we have recently found a body hitherto unknown, the β,γ-hexenol ester of phenylacetic acid. The ester is remarkable by its strange, most lasting smell, and occurs in the fractions boiling between 250 and 310°. On saponifying these fractions with alcoholic potash, phenylacetic acid and hexylene alcohol result. The latter, on close investigation, was not identical with the α,β-hexenol such as found in the green leaves of numerous plants by Curtius and Franzen, but revealed itself as β,γ-hexenol $CH_3 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH_2OH$. The position of the double linking was manifested by the results of oxidation, potassium permanganate leading to propionic acid, and chromic acid to α,β-hexylenic acid. The latter appeared, by transposition of the double bond on saponification, in accord with Fittig's observations, from the hexenyl ester of β,γ-hexylenic acid formed primarily by oxidation.

β,γ-Hexenol has the following constants: — b. p. 55 to 56° (9 mm.), 155 to 156° at mean atmospheric pressure; d_{15° 0.8508; α_D — 0°10′; n_{D20° 1.48030. It adds two atoms of bromine. The smell reminds, in great dilution, of grass and fresh green leaves.

The following derivatives were prepared from the hexenol from Japanese peppermint oil: —

Hexenyl phenylacetate $C_{14}H_{18}O_2$. B. p. 135 to 136° (4 mm.), 299° (760 mm.); d_{15° 1.000; $\alpha_D \pm 0$; n_{D20° 1.49810.

Hexenyl benzoate $C_{13}H_{16}O_2$. B. p. 134 to 135° (6 mm.); d_{15° 1.0083; $\alpha_D \pm 0$; n_{D20° 1.50560.

Hexenyl acetate $C_8H_{14}O_2$. B. p. 76 to 76° (23 mm.); d_{15° 0.9077; $\alpha_D \pm 0$, n_{D20° 1.42355.

Hexenyl formiate $C_7H_{12}O_2$. B. p. 66° (35 mm.); d_{15° 0.9149; $\alpha_D \pm 0$, n_{D20° 1.42685.

Hexenyl α-naphthylurethane $C_{17}H_{19}O_2N$, m. p. 70 to 71°.

Hexenyl acid phthalate $C_{14}H_{16}O_4$, liquid, yielding a well-crystallizing silver salt melting at 126°.

In this connection, we report on the synthesis, performed by us some time ago, of the aldehyde corresponding to the above-mentioned α,β-hexylene alcohol, the

[1]) *Report* October **1890**, 61. For later investigations, see *Report* October **1916**, 41. — [2]) *Yakugakuzasshi* **1916**, No. 415; *Apotheker Ztg.* **32** (1917), 556.

so-called leaf-aldehyde. We followed the method of P. Sabatier and A. Mailhe[1]) devised for the preparation of saturated aldehydes, by catalytic reduction of α,β-hexylenic acid with formic acid in presence of heated manganese protoxide. We mixed four parts of hexylenic acid with six parts of formic acid and conducted the vapour of this mixture in a combustion tube over manganese protoxide heated to about 350°. The oil collecting in the receiver was dissolved in ether and washed first with water, then with sodium carbonate solution and dried with dry sodium sulphate. The crude aldehyde thus obtained boiled in the main between 46 and 60° (4 mm.); by transforming it into the *m*-nitrobenzhydrazone, m. p. 167 to 168°, we could prove the presence of Curtius and Franzen's leaf aldehyde. Its semicarbazone melted at 172 to 173°; it was prepared by treating 5 g. of the distilled crude aldehyde with 5 g. semicarbazide hydrochloride and 5 g. sodium acetate over night and crystallizing the crude semicarbazone, after washing with water, repeatedly from alcohol. For the preparation of the *m*-nitrobenzhydrazone, 6 g. of the crude aldehyde were dissolved in a little alcohol and the solution mixed with 3 litres of water; to this mixture there was added, with stirring, a hot solution of 8 g. *m*-nitrobenzhydrazide. After 4 hours' stirring, 17 g. of the hydrazone had separated which, after recrystallizing four times, showed the melting point as given above, and as found also by Curtius and Franzen.

On this occasion, we prepared also the *m*-nitrobenzhydrazone of hexylic aldehyde; m. p. 115 to 116°.

Official estimates show that Japan had a normal peppermint crop in 1916[2]). The exports were 936882 kin[3]).

Some time ago, we mentioned that the Japanese parliament was said to be occupied with drawing up a law, permitting of an efficient state control of the peppermint industry[4]). Since then, we have not heard anything else on the subject. We gather, however, from a more recent number of a periodical[5]) that the competent circles in Japan are convinced that it is necessary to improve the organization of the peppermint industry. It is planned to make the peppermint growing and the manufacture of menthol more rational in Hokkaido, by building distilleries in the chief producing districts, in which the crude oil can be treated further, instead of sending it to Yokohama or Kobe.

The dementholized oil, left behind in the refining process, finds increasing use abroad. Previous to the war, Germany was the most important customer for menthol, whereas now America takes up at least 88 per cent. of the total production. The figures mentioned for the 1916 production; *viz.*, 525000 lbs. to the value of $ 1031250, surely refer to menthol.

As to the cultivation of peppermint, see pages 79 and 80 of this *Report*.

Petit-grain Oil. It is the chief article of direct export from Paraguay to the United States. As per a communication from the American Consulate at Asuncion, 23040 lbs. to the value of $ 35416 were exported in 1915 and 33680 lbs. worth $ 60496 in 1916. During the six first months of 1917, the figures were 22677 lbs. to the value of $ 45043, as compared with $ 24283 in the same period of the previous year[6]).

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[1]) *Compt. rend.* **158** (1914), 985. — [2]) *Der Neue Orient* **2** (1918), 380. — [3]) It is not quite clear to what this refers, perhaps to peppermint oil. Our repeated enquiries, addressed to the editors of the periodical, have remained unanswered. — [4]) Comp. *Report* April **1915**, 33. — [5]) *Monthly Trade Journal; Journ. of Ind. and Eng. Chemistry: Americ. Journ. Pharm.* **91** (1918), 221. — [6]) *Chemist and Druggist* **89** (1917), 825.

Pine Needle Oils. A sample of Siberian pine needle oil offered to sale last year proved to be a worthy successor to the makeshifts dealt with here two years ago[1]), which were marketed as genuine oils, although being utter failures.

The oil in question behaved as follows: — d_{150} 0.8840; α_D — 0°9′; ester content (calc. for bornyl acetate) 5.9 per cent.; soluble in about 4 and more vol. of 90 per cent. alcohol. The great difference from genuine oil became manifest when comparing it with the constants of the latter oil: — d_{150} 0.905 to 0.925; α_D — 37° to — 43°; ester content, 29 to 40 per cent.; soluble in 0.5 to 1 vol. 90 per cent. alcohol. In smell, too, there was not the least resemblance. Probably, the mixture contained a heavy amount of pine tar oil.

It is astonishing that such stuff still finds purchasers.

Aleppo Pine Needle Oil.—This oil, when genuine, does, according to Tsakalotos[2]), not show lævorotation, as is stated in Gildemeister's text-book (2nd German ed., vol. II, p. 133; 2nd English ed., vol. II, p. 127), but is dextrorotatory. The genuine oil consists largely of *d*-pinene, a sample from Attica was found to have $[\alpha]_D + 39.4°$. The statement in Gildemeister and Hoffmann's book is, in Tsakalotos' opinion, due to a confusion with the oil of *Pinus maritima*, Mill.

We are obliged to reply that can be no question of such an erroneous statement on *our* part, since the data given in Gildemeister's book concerning the lævorotation were taken from Belloni's[3]) work entitled, "sull' essenza di gemme di *Pinus maritima*, Mill." Now the latter name is synonymous to *Pinus halepensis*, Mill., the Aleppo pine. A mistake can have happened merely to Belloni in confounding *Pinus maritima*, Mill. with *P. maritima*, Poir.

The oil of turpentine from the Aleppo pine is also dextrorotatory: — $[\alpha]_D + 47$ to 48°.

Rosemary Oil. See page 82 of this *Report* on rosemary oil from British East Africa.

Otto of Roses, Anatolian. The production of rose oil in Turkey (?) in 1917 has not been brilliant, as the German Consul General in Constantinople reports under September 21st 1917[4]). In some districts it has been impossible to gather the flowers in time for lack of hands. In addition, fire-wood was scarce owing to the rise in prices. As the distillation was thus reduced, it is estimated that the total production of rose oil is one third smaller than in the previous year. One reckons with only 40000 to 50000 miskals (1 miskal = 1½ dram). As the flowers were good, the quality of the oil is likewise so.

Comparatively little has been exported so far, owing to the difficulties of transport. The stocks in Constantinople from old crops and the new one together are estimated at 150000 miskals, those at Smyrna also at 150000 miskals and those in the interior at 100000 miskals, so that 400000 miskals would be available in Turkey.

In spite of the small exports, prices have gone up considerably, especially because circles that otherwise have had nothing to do with rose oil, have seized this article as a suitable investment for speculation. The prices range at present between 30 and 50 piasters per miskal.

Otto of Roses, Bulgarian. During the last years, rose growing has gone down in Bulgaria instead of increasing, as the peasants prefer growing indian corn instead[5]).

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[1]) *Report* October **1916**, 45. — [2]) *Gazz. chim. ital.* **47** (1917), I. 285; *Journ. chem. Soc.* **112** (1917) I. 577. — [3]) *Annuario della Soc. chim. di Milano* **11** (1905), *fasc.* 6; *Chem. Zentralbl.* **1906**, I. 360. — [4]) *Nachr. f. Hand., Ind. u. Landw.* **1917**, No. 83, page 3. — [5]) *Bulgarische Handelszeitung; Die Seife* **2** (1917), No. 18, page 7.

The cultivation of roses causes considerable costs, whereas the prices obtained for the produce are comparatively low and do not even cover the expenses in bad years. However, it must be taken into consideration that the growers generally distil the roses themselves and are unable to do it to the full advantage, owing to their mostly primitive installations. Some of the rose oil dealers get the product from the second or third hand, but even then at prices that are in no proportion with the producers, costs and the value of their labour. The producers are thus induced to increase their quantities through adulteration, and their disappointment with this state of affairs is one of the causes of the decline of this Bulgarian industry, unique in its kind, and which in many villages of the Strema and Tunsha valleys is the only source of income, as the soil is too poor there for corn and still more for rice, tobacco and poppies.

In order to save the declining cultivation of roses, some intelligent and influential producers of rose oil undertook to unite all those interested in the article with the aim of mutual assistence. This league has now 5000 members, half of which are collective ones, *i. e.* companies. As per the statutes, the tasks of the league are the following: 1. to secure cheap credit for its members; 2. to abolish adulteration; 3. to organize joint distillation; 4. to supply the companies with all that is needed for the production of rose oil.

For this purpose, the help of some financial institute is required, and it is the newly founded "Rozowa Banka" (Rose Bank) who undertakes to foster the endeavours of the league.

The purchases of rose oil from the producers will have to be made through the mediation of the league and under the control of chemists and experts. The league will fix the price every year, granting the producers an adequate profit. The price thus fixed is absolutely binding for the bank. All adulteration of rose oil is prohibited and causes the perpetrator to be excluded from the league.

We read in another journal[1]) that local taxes on rose oil are planned in Bulgaria. The Home Office has drawn up a law entitling town and village authorities to levy a tax of $^1/_2$ per cent.[2]) on the rose oil produced in their district.

Sage Oil. As to the cultivation of sage, see page 79 of this *Report*.

Sandalwood Oil, East Indian. We reported before on the sandalwood distilling plant in Mysore on account of several short notices gathered from periodicals[3]). The Imperial Institute[4]) has now published an article on this undertaking, containing besides some statistical data regarding the production of sandalwood oil[5]).

It is estimated that Mysore supplies about seven tenth of the world's consumption of sandalwood. Previous to the war, 52 per cent. of the exports of sandalwood from British India where destined for Germany, 18 per cent. for the United States and 10 to 20 per cent. for Great Britain. The value of the exports was 128626 £, in 1913/14, Germany's share in it being 56303 £, that of Great Britain 28326 £ and that of the United States 20454 £.

In the two last years before the outbreak of the war, the price of sandalwood in Mysore had doubled, which was to be explained on the one side by the "spike" disease and on the other by the fact that the Government only released 2500 tons for sale, equal to the yearly requirements of the whole world.

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[1]) *Deutsche Levante-Zeitung* 8 (1918), 223. — [2]) Of the value? — [3]) Comp. *Report* October **1916**, 51. — [4]) *Bull. Imp. Inst.* **15** (1917), 108. — [5]) See *Report* October **1913**, 95.

As the sandalwood trade came to a standstill after the outbreak of the war, owing to the absence of Germany's demand, the Mysore Government decided upon distilling the wood originally meant for export. A distilling plant was erected in the neighbourhood of Bangalore, capable of producing 2000 lbs. of oil per month, in the beginning, but this monthly production was raised up to 5000 lbs. later on. A second plant is now in the course of construction, the output of which is intended to be about 20000 lbs. per month. The oil obtained in the Government factory answers the requirements of the British and other pharmacopoeiæ. The price obtained for it in London, in 1916, varied between 29/- and 50/- per lb. Each consignment is accompanied by a Government certificate re purity. As in the United States sandalwood oil has to pay duty at the rate of 20 per cent. *ad valorem*, it seems questionable whether the Mysore oil will be marketable in America.

Owing to the high prices of sandalwood, substitutes are being imported into British India. The imports of such were as follows:—

origin	1910/11	1911/12	1912/13	1913/14	1914/15
West-Australia . . .	3221 £	4678 £	5208 £	9478 £	5110 £
Straits Settlements . .	2748 „	2680 „	3903 „	3699 „	2518 „
other countries . . .	707 „	768 „	2596 „	399 „	744 „
total:	6576 £	8126 £	11707 £	13576 £	8372 £

The quantities here ascribed to the Straits Settlements originated in part from West Australia.

China imported the following quantities of similar wood:—

origin	1910	1911	1912	1913	1914
Hongkong . . .	6092 tons	5815 tons	3716 tons	4753 tons	4823 tons
Australia . . .	338 „	602 „	1564 „	— „	2217 „
other countries .	364 „	167 „	3 „	240 „	271 „
total:	6794 tons	6584 tons	5283 tons	4993 tons	7311 tons

The quantities given for Hongkong refer in part to wood imported from Australia and reexported.

The sandalwood from Australia comes mostly from *Fusanus spicatus* R. Br. West Australia exported the undermentioned quantities of such wood:—

1910	1911	1912	1913	1914	1915
70775 £	85506 £	27533 £	47589 £	65919 £	88556 £

South Australia exports small quantities of sandalwood from *Fusanus acuminatus*, R. Br., called *"Quandong"*.

In the cultivation of the sandal tree, due attention must be given to its half parasitic way of living. In India, 144 different host plants are known, all trees, 27 of which belong to the leguminous plants. It will be difficult, perhaps, to find the proper host plants elsewhere; however, the tree has been planted with success in Mauritius[1]). The leguminous plants *Pongamia glabra*, Vent., and *Albizzia Lebbek*, Benth., come into consideration as host plants. The sandal tree grows slowly, it being possible to obtain the wood from it only when it is 20 to 40 years old.

We gather from a periodical[2]) that, in 1916, Madras exported 40000 lbs. of oil, the lion's share of which went to Great Britain.

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[1]) Comp. *Report* April **1915**, 41. — [2]) *The Oil and Colour Trades Journal: Handelsberichten (Den Haag)* **11** (1917), 447.

According to a notice published elsewhere[1]), the Madras ports were responsible for nearly 4000 gallons, in 1916/17, to the value of 10 £ per gallon, whereas the Indian exports of wood totalled 128626 £ in 1913/14, 35918 £ in 1915/16 and 126016 £ in 1916/17.

Star anise Oil. The report of the American consul at Saigon[2]) mentions star anise oil. The exports of the ten last years oscillated between 40 and 100 tons to the value of 18000 and 43000 £, respectively. The relative figures for the years from 1913 to 1916 were: —

1913	.	.	.	230	tons	to the value of	100000	£
1914	.	.	.	48	„	„ „ „ „	22750	„
1915	.	.	.	74	„	„ „ „ „	31690	„
1916	.	.	.	50	„	„ „ „ „	15000	„

Storax Oil. The imports of oriental storax into the United States having ceased owing to the war, the interest in American storax or sweet gum from *Liquidambar styraciflуum*, L. *(Hamamelidaceæ)* has risen. It appears, however that unadulterated products are scarcely to be had, for out of 12 trade samples investigated by S. Jordan[3]), not a single one came up to the requirements to be formulated for American storax. The adulterants recognized were, among others, rosin, castor oil and exhausted storax.

Genuine American storax, in a fresh state, is a clear, yellowish brown, semiliquid, honeylike mass; the purified material is a little more viscous. Old, solidified storax is collected in some places and used as chicle gum. An authentical sample, collected in Durham County, North Carolina, in March 1917, showed the following constituents: 22.37 per cent. of essential oil, 0.32 per cent. of ashes, 5.24 per cent. of bodies insoluble in alcohol, 22.86 per cent. of cinnamein, 34.76 per cent. of resinous esters, 2.11 per cent. of resinous acid, 12.65 per cent. of free cinnamic acid and 28.02 per cent. of free acid. The acid value was 68.7, the ester value 62.9.

Turpentine Oil. The analyst often has to examine oil of turpentine as to the presence of light petroleum and other hydrocarbons of similar origin, but it occurs far more seldom that he is called upon to prove the presence of turpentine oil in light petroleum. However, the disagreeable odour of unsufficiently purified light petroleum is covered sometimes by adding small quantities of turpentine oil, wood turpentine oil or allied products and, as J. Formánek communicates in a treatise published together with J. Knop and J. Korber[4]) in some cases even nitrobenzene. In order to prove the presence of turpentine oil in light petroleum, a test with bromine or iodine solution is recommended, when, in the absence of oil of turpentine, the liquid coloured through the bromine or iodine remains unchanged for some while, whereas the brown colour disappears at once or within a very short time, if oil of turpentine is present. Formánek ascertained through numerous experiments that this test is not decisive at all for motor spirits, as they contain almost all, especially if not, or unsufficiently, refined, various compounds (aromatic or unsaturated hydrocarbons) which take up bromine, so that such motor spirits discolour bromine solution at once or after a very short interval. Iodine being absorbed far more slowly by such compounds in the cold, iodine solution is better fit to be used when testing for turpentine oil, but with a certain reserve, as some sorts of light petroleum may contain

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[1]) *Times Tr. Suppl.*, February **1918**; *Wirtschaftlicher Nachrichtendienst*, published by the *Deutscher Überseedienst* **4** (1918), 630. — [2]) *Perfum. Record* **8** (1917), 307. — [3]) *Journ. of Ind. and Eng. Chemistry* **9** (1917), 770. — *Americ. Journ. Pharm.* **89** (1917), 581. — [4]) *Chem. Ztg.* **41** (1917), 730.

compounds which quickly absorb even iodine, so that in such cases a discolouration would take place, although no oil of turpentine might be present. If a drop of Waller-Hübl's[1]) solution be added to 5 cc. of light petroleum containing turpentine oil and the mixture shaken, the pink colouring will disappear in a comparatively short time whereas it is maintained that pure light petroleum remains coloured even after half an hour's time. The author compiled in the form of tables the results of testing several refined and unrefined light petroleums by means of bromine and iodine. They show that iodine solution may be discoloured in less than 30 minutes, even if no turpentine oil is present. Most probably the discolouring depends more upon the aliphatic unsaturated hydrocarbons than upon the aromatic ones.

In any case, the methods for ascertaining the presence of oil of turpentine are only indirect and uncertain, but the iodine solution may serve as a criterion for the presence of unsaturated hydrocarbons.

Klingmüller[2]) reports on the treatment of inflammations and abcesses by injecting turpentine. The turpentine[3]) is capable of influencing favourably inflammations and suppurations, caused by various germs. Subcutaneous or intramuscular injections of 0.1 to 0.2 grams of turpentine in a 20 per cent. olive, arachid or almond oil solution were given once or repeatedly. Excepting unimportant local irritation, no injurious by-effects were noticed. The effect was specially favourable in the case of purulent secretions with gonorrhœa of the urethra and of the conjunctiva, furthermore with gonorrhoical arthritis and tendovaginitis. Besides, *staphylomycoses*, *pityriasis rosea*, *lichen ruber*, *impetigo contagiosa* and catarrhs of the bladder were influenced favourably.

Wederhake[4]) recommends treating puerperal fever according to the old method with oil of turpentine as intragluteal injections of 1.5 cc. of a 20 per cent. turpentine oil solution[5]) every fifth day, combined with a subcutaneous injection, every three hours, of 5 cc. of *ol. camphor. fort.*

We have reported already before on the application of oil of turpentine in treating wounds[6]).

A. Woodmansey[7]) when studying the influence of several diluents (thinners) on the drying property of linseed oil, has likewise given his attention to the effect of drying substances (driers) on oil of turpentine, especially red lead and manganese resinate. He filled two beakers with 25 cc. each of turpentine oil (b. p. 156 to 163°; d 0.864), added to the one 0.7488 grams of red lead and allowed the contents to evaporate in a dustfree atmosphere. The weights of the turpentine oil were as follows:—

	without addition	with addition of red lead
after 20 days	11.2019 grams	13.8739 grams
„ 29 „	7.1578 „	10.3709 „
„ 49 „	1.5708 „	6.9454 „

For the experiments with manganese resinate, turpentine oils of different origin were used, but it would lead us too far to copy the results, which are chiefly of interest for varnish manufacturers.

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[1]) A solution of iodine and mercury dichloride in alcohol of 95 per cent., to which some hydrochloric acid has been added. — [2]) *Deutsche medizin. Wochenschr.* **43** (1917), 1294; *Therap. Monatsh.* **32** (1918), 19. — [3]) It is not evident from the treatise, whether turpentine or, what would seem more probable, oil of turpentine, is meant. — [4]) *Zentralbl. f. Gyn.* 1917, 843; *Therap. Monatsh.* **31** (1917), 492. — [5]) The solvent is not named. — [6]) Comp. *Report* October **1916**, 107. — [7]) *Journ. Soc. chem. Industry* **36** (1917), 1253.

L. Paul[1]) published an article on fossile resins, in which he discusses the formation and composition of these intricate bodies. However, as it does not lend itself to being curtailed, we refer our readers to the original.

The *"Kriegsausschuss für pflanzliche und tierische Öle und Fette"*, Berlin[2]) gives some particulars as to the native production of resin. As they will interest only a limited number of our readers, we mention the article for the sake of completeness, without going into details. For previous communications on the subject, we beg to refer to our *Reports* of October **1915**, 37; October **1916**, 52; October **1917**, 62.

At the same time, we would call attention to a collection of articles by C. von Tubeuf[3]) on the present state and the prospects of the production of resin and to allied publications by Münch[4]), Gundel[5]), Auerochs[6]), Koehl[7]), Wislicenus[8]) and Kienitz[9]).

As to the optical rotation of the turpentine oil of the Aleppo pine, see page 41 of this *Report*.

An unexpected demand predominates for so-called Swedish oil of turpentine, whether crude or pure, whether obtained by dry distillation or by the sulphite process, in consequence of there being no imports of American turpentine oil. The active trade thus created makes it necessary to have an adequate method of analyzing the crude oils, for which reason J. Klinga[10]) compiled a review of all existing tests. The following way is the most suitable: 150 c. c. of the crude oil are distilled from a short-necked vessel, provided with a fractionating tube according to Young and connected with a Fagerlind condenser, the distillate being collected in a graduated cylinder. Giving due attention to a uniform rate of distillation and protecting the apparatus against draught, the oil is separated into a first fraction up to 150° and a second fraction from 150 to 180°. The distillation is interrupted at 180°. The rate of distilling is 3 to 4 c. c. per minute. The second fraction is then shaken with a 10 per cent. sodium lye and the reduction of volume ascertained. The volume of the part insoluble in sodium lye may then, with sufficient exactitude for most requirements, be designated as proportional with the content of "oil of turpentine" in the crude oil.

There cannot be a question here of "oil of turpentine" in the real meaning of the term, at the most of a similar product.

For many years already, there has been a tendency in British India to become independant of foreign countries with regard to turpentine products. For this purpose, early attempts have been made to exploit the native pine woods, consisting especially of *Pinus longifolia*, Roxb., on which subject we have reported regularly[11]). The latest achievements in this domain, and the present state of the Indian turpentine industry generally, are now described in detail in a publication of the Imperial Institute[12]). The most important turpentine producing districts are West-Almora, Naini Tal and the East Almora Divisions of the Kumaun region. At Bhowali in Naini Tal, there is a Government plant for the production of oil of turpentine and rosin. Another resin producing part is the Punjab, where recently a distilling plant has been erected at Jalloo. The rosin obtained at Bhowali is consumed chiefly by Indian paper mills, the turpentine oil[13]) by the railways.

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[1]) *Die Seife* **2** (1918), N°. 20, page 5, &c. — [2]) *Die Seife* **2** (1917), N°. 22 of November 28th. — [3]) *Naturwiss. Zeitschr. f. Forst- u. Landwirtsch.* **16** (1918) 2, 78. — [4]) *Ibidem*, 18. — [5]) *Ibidem*, 28. — [6]) *Ibidem*, 35. — [7]) *Ibidem*, 43. — [8]) *Ibidem*, 53. — [9]) *Ibidem*, 61. — [10]) *Bihang till Jern-Kontorets Annaler* **18** (1917), N° 1, page 29; *Deutsche Parf.-Ztg.* **3** (1917), 107. — [11]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 82. — [12]) *Bull. Imp. Inst.* **15** (1917), 544. — [13]) The original says "turpentine".

The following tables show the imports of oil of turpentine into India during the years 1912/13 and 1916/17. The largest quantity is supplied by Great Britain, but it is mostly of French or American origin.

Imports of oil of turpentine into British-India:

		1912/13	1913/14	1914/15	1915/16	1916/17
total quantity	cwts.	20 779	16 050	11 788	7 220	6 608
total value	£	30 630	28 319	22 531	14 175	17 407
origin:		cwts.	cwts.	cwts.	cwts.	cwts.
Great Britain		18 818	13 485	8 962	7 034	6 309
other British countries		379	1	2	27	2
United States		1 559	2 488	2 790	138	294
Germany		21	74	—	—	—
other foreign countries		2	2	34	21	3

There occur five kinds of pines in India, *viz.*,

Pinus longifolia, Roxb. (*Chir* pine), growing in the Himalaya and Siwalik mountains, as well as in the valleys of the most important Himalaya rivers, in an altitude of from 1500 to 7500 feet. It is found as far west as Afghanistan and eastwards as far as Bhutan[1]).

Pinus excelsa, Wall., (*Kail* or blue pine) occurs in the temperate zones of the Himalaya mountains in an altitude of 6000 to 12500 feet. It is spread over almost the same districts as *Pinus longifolia*, but it does not occur in Northwest-Kumaun and in Sikkim.

Pinus Khasya, Royle, (*Dingsa* or *Khasia* pine) is found in a height of 3000 to 7000 feet on the Khasi Hills, on the hills of Lushai country, Chittagong (Assam), on the Shan Hills and the Martaban Hills in Burmah.

Pinus Merkusii, Jungh et de Vriese *(Tinyu)* is a predominantly Burmese kind, growing in the hilly woods of the Shan states and Tenasserim at an elevation of from 500 to 3500 feet.

Pinus Gerardiana, Wall. (*Neosia* or Himalaya edible pine) occurs in isolated districts of the inner, dry, unfertile parts of the western Himalayas.

There may be about 2068530 acres covered with *Pinus longifolia*, excluding the regions of Sikkim, Bhutan, Nepal, Maudi, the boundary states and Afghanistan.

In British India, there are about 128000 acres with *Pinus excelsa*.

The first attempts to produce turpentine oil and rosin were made about 1890 in Dehra Dun. About 1895, it was established that *Pinus longifolia* yielded turpentine in sufficient quantity to make the work pay and that there was a market for rosin and oil of turpentine. In the following year, a distilling plant was erected in Bhowali, which was enlarged in 1914/15 and is still working. A second installation is to be built in the neighbourhood of Tanakpur. In the beginning, the new industry developed but slowly, the yield of crude turpentine being 125 tons in 1903/04 and 515 tons in 1911/12. But as soon as it had been ascertained that tapping the trees did not harm them, steps were taken in order to make the industry develop quickly. The production the was 971 tons in 1912/13, 1580 tons in 1913/14, 1768 tons in 1914/15 and 2089 tons in 1915/16.

The Bhowali works produce 4 different grades of turpentine oil, the keenest demand being for grade 3. In 1913/14, 477 tons of turpentine oil were exported to Java.

The main difficulty for the industry in Kumaun consists in the transport of the crude turpentine to the distilling plant, the places where it is collected frequently being 100 miles off.

[1]) Comp. *Report* October 1917, 71.

In the Chakrata district, turpentine was likewise obtained until a very short while ago, the output being 50 tons in 1915/16. There is a distilling plant in Kalsi, but the stills are antiquated and out of use since 1914.

In the Punjab, resin is obtained from the Rawalpindi forests. The woods in Kangra, however, in the north-east part of the province, are not exploited any longer. *Pinus longifolia* supplies the resin in the Punjab too, whereas the experiments with *Pinus excelsa* have not given any satisfactory results. The yield was scanty and, besides, the woods are too much out of the way.

The exploitation of the Kangra woods was begun in 1897/98 and in 1899 a factory was built in Nurpur which worked for 5 or 6 years, consuming 150 to 180 tons of resin annually and producing 110 to 150 tons of rosin, in addition to 7000 to 9000 gallons of turpentine oil.

Tapping in the Rawalpindi forests started in 1909/10. In the year following, a distilling plant was erected in Shahdara, on the Ravi river, 4 miles north of Lahore, where it was possible to distil 367 tons yearly. In 1914, this factory was badly dammaged by floods, in consequence of which it was transferred to Jalloo, about 9 miles to the west of Lahore, a completely new factory being built there according to the French type[1]). This factory consumed 717 tons of turpentine, in 1915/16, obtaining 447 tons of rosin and 31445 gallons of turpentine oil.

Although there are considerable pine woods in Assam and Burmah, tapping has not been tried there so far.

In India, the trees are tapped according to the French method. One starts about March and renews the wound about 5 times a month during the whole summer. The trees are tapped for 5 consecutive years and then left in peace for 10 years, so that always only one third of the trees are under exploitation. Generally speaking, the trees in Kumaun are only slightly tapped; trees of 3 feet 6 inches to 4 feet 6 inches in circumference are bored but once, those of 4 feet 6 inches to 6 feet, twice, and those over 6 feet, three times. Trees destined to be cut down within 5 years are tapped to exhaustion, the number of boring holes being increased sometimes up to eleven. 2000 trees, tapped to exhaustion, yielded 450 cwts. of turpentine, in 1913, whereas with the ordinary slight tapping not more than 120 cwts. would have been obtained.

The same method is worked upon in the Punjab, but it has been found out there that it is advantageous to scrape the wound, which is done now every 4 or 5 days.

The American way of distilling over an open fire is not appropriate for the turpentine of *Pinus longifolia;* it must be distilled with steam, as it is customary in France. The turpentine is first melted through heating with steam, and in order to facilitate the process a little turpentine oil of the previous distillation is added. Dust and other impurities are then allowed to deposit and the pure turpentine is drawn off in storing vessels from which the stills are filled in adequate quantities. The stills are surrounded by steam and can be brought up to the desired temperature by means of overheated steam. The turpentine oil distilling over with the steam is conducted through a second still, inserted between the proper still and the condenser, in order to free it from the particles of turpentine and rosin that may have been carried over. In the condensed distillate, the oil of turpentine and the water are separated mechanically. The oil is then rectified and treated with lime water in order to remove the traces of resinous acids that it may contain. Formerly, it was freed from water by means of sodium sulphate, but nowadays it is only allowed to stand in huge tanks, when the water

[1]) Comp. *Report* October **1916**, 56.

deposits by itself. It is now being tried to avoid the rectification by fractionation in the course of distilling.

One expects the Bhowali plant to be in a position within a few years' time to cover 60 per cent. of the Indian consumption of oil of turpentine and of 80 per cent. of that of rosin.

In Bhowali, 17.5 to 19 per cent. of oil are obtained from the turpentine of *Pinus longifolia*, the quality and the age of the resin being responsible for the variation in yield.

It will perhaps be remembered that, a few years back, we discovered in our laboratories in the turpentine oil of *Pinus longifolia* a hydrocarbon that, on being treated with gaseous hydrochloric acid, yielded sylvestrene dichloride and which we considered for that reason as identical with sylvestrene[1]). Robinson[2]), who likewise investigated the oil, presumes that sylvestrene may perhaps not be present as such in the oil, but that this contains a hydrocarbon which, it is true, forms with hydrochloric acid gas a derivative of sylvestrene, but differs from it nevertheless.

This terpene has been examined more closely in the Imperial Institute. After having been purified through distillation, it boiled at 173°; $d_{15°}$ 0.867; $[\alpha]_D + 12° 20'$. In contact with the air, it oxidized far more quickly than α-pinene. A part, purified through fractionated distillation until the optical rotation was constant, was cooled down with liquid air, when the crystals and the mother-lye thus obtained showed again the same rotatory power. On being treated with gaseous hydrochloric acid, the terpene yielded sylvestrene dihydrochloride, but there was not the characteristic blue colouring with acetanhydride and concentrated sulphuric acid. Besides, the specific gravity is rather high for sylvestrene. This shows that this body is a uniform terpene, not described so far and which differs from sylvestrene, as Robinson presumed. Perhaps it contains still other terpenes which can be separated off only with difficulty.

We obtained at the time the sylvestrene dihydrochloride from a terpene fraction which we had treated with potassium permanganate in order to prove the presence of β-pinene. The fraction that yielded the dihydrochloride boiled between 174 and 176° under ordinary pressure: $d_{15°}$ 0.8713; $\alpha_D + 8° 30'$; $n_{D20°}$ 1.47323.

Constants of sylvestrene and of the allied terpene from Indian turpentine oil.

Sylvestrene (Wallach)	b.p. 175 to 176°	$d_{20°}$ 0.848	$[\alpha]_D + 66.32°$	n_D 1.47573
New terpene (Imp. Inst.)	b.p. 173°	$d_{15°}$ 0.867	$[\alpha]_D + 12° 30'$	
„ „ (Schimmel & Co.)	b.p. 174 to 176°	$d_{15°}$ 0.8713	$[\alpha]_D + 8° 30'$	$n_{D20°}$ 1.47323

At the and of the publication the possibility is discussed of exporting Indian oil of turpentine to Great Britain. This country imported the following quantities: —

Imports of oil of turpentine into Great Britain.

	1912	1913	1914	1915	1916	1917
total quantity . . . cwts.	656 216	560 330	348 206	529 517	430 780	221 192
„ value . . . . £	1 028 007	768 800	542 205	903 381	903 384	620 747
origin:	cwts.	cwts.	cwts.	cwts.	cwts.	
British countries	38	—	—	—	—	
United States	575 131	476 400	249 509	418 050	368 575	
France	17 986	33 656	19 491	40 506	5 229	
Russia	48 713	32 648	21 006	3 899	—	
Germany	3 073	5 293	2 914	—	—	
other foreign countries .	11 275	12 333	10 286	67 062	56 976	

[1]) *Report* April **1911**, 117. — [2]) *Proceed. chem. Soc.* **27** (1911), 247; *Report* April **1912**, 124.

In connection with this, we beg to mention a communication from the Egyptian Gazette of May 20th[1]), according to which the Imperial Institute has been able to state that British varnish manufacturers, who had had an opportunity to try Indian turpentine oil on a large scale, are completely satisfied with its quality. It might be expected, therefore, that it would soon fetch, in Great Britain, the same price as the American product, now quoted at 124 s. per cwt. The prospects would be equally favourable for the sale of Indian rosin in Great Britain. The quantity now available might be estimated at several thousand tons, the price being up to 56 £ per ton.

The Italian oil of turpentine is no more a distillate from a uniform plant material than the American product, but consists of a mixture of the oils of *Pinus Pinea* L., and *P. Pinaster*, Sol. F. C. Palazzo[2]) reported already previously on the properties of the oil of authentical resin collected in Italy from *Pinus Pinea*. M. Palazzo[3]) now describes the pure oil of Italian turpentine from *Pinus Pinaster*. It shows a somewhat higher rotation than French turpentine oil, which likewise comes from the maritime pine. The oil obtained by himself had the following properties: $d_{15°}$ 0.856 to 0.857, α_D — 37.3 to — 37.7°, $n_{D25°}$ 1.4653 to 1.4655, point of inflammation 32.5°. It contained an ample proportion of α-pinene.

Palazzo further gives the following particulars: for a commercial oil, a mixture of the oils from both kinds of *Pinus* = $d_{15°}$ 0.863, α_D — 48.15°, $n_{D25°}$ 1.4678; for a technical oil = $d_{15°}$ 0.867 to 0.871, α_D — 35°, $n_{D25°}$ 1.4700 to 1.4707.

A French periodical[4]) publishes a collective report of the turpentine oil trade, the most important adulterants and substitutes and the legal measures against fakers, etc. As the article does not contain any fresh points of view, it will suffice just to mention it.

O. M. Halse and H. Dedichen[5]) have shown that the so-called sulphate turpentine oil, a by-product of the manufacture of cellulose, contains α- and β-pinene. The sulphite turpentine oil[6]), as Halse and S. Samuelsen[7]) have been able to determine, likewise contains α-pinene, in addition to a small quantity of β-pinene. They call the product "Norwegian wood turpentine oil".

W. Dahse[8]) reports on the refining of wood turpentine oil, giving a summary of the numerous, mostly patented methods which have been recommended for the purification of the product. The task undertaken by the author is most opportune, given the present scarcity of turpentine oil and similar products.

Thyme Oil. Canals[9]) tried to ascertain in how far the formation of the essential oil in the plant is influenced by the different solar rays. For this purpose, he grew thyme plants under a frame with various kinds of stained glass. When testing the stained glass spectroscopically, he had found that the red glass let through rays of λ 0.7800 to λ 0.6060 μ and the blue glass those of λ 0.5820 to λ 0.4045 μ length of

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[1]) *Nachr. f. Hand., Ind. und Landw.* **1918**, N° 74, p. 4. — [2]) *Annali Chim. appl.* **6** (1916), 135; *Journ. Soc. Chem. Industry* **35** (1916), 1122; *Report* October **1917**, 72. — [3]) *Annali Chim. appl.* **7** (1917), 88; *Chem. Zentralbl.* **1917**, II. 631. — [4]) *Ann. des Falsifications* **10** (1917), 33; *Chem. Zentralbl.* **1917**, II. 137. — [5]) *Berichte* **50** (1917), 623; *Report* October **1917**, 73. — [6]) Comp. Z. Kertész, *Chem. Ztg.* **40** (1916), 945; *Report* October **1917**, 74. — [7]) *Tidsskr. for Kemi* **1918**, N° 11, p. 177 and 178; *Apotheker-Ztg.* **33** (1918), 258. — [8]) *Deutsche Parf.-Ztg.* **4** (1918), 100. — [9]) *Bull. Soc. chim.* IV. **21** (1917), 204.

waves. The thyme plants all came from one and the same spot of the Garrigue mountains in the neighbourhood of Montpellier. They were divided into four sets: —

a) first set, planted in a frame under colourless glass;
b) second set, planted in a frame under blue glass;
c) third set, planted in a frame under red glass;
d) fourth set, left on the spot.

After 10 days, the plants of set a) showed a few flowers already, wheras those of b) and c) still looked sickly, especially those under the red glass.

Another 10 days later, the a) plants all had flowers and not a single one had died. The leaves were somewhat larger than those of the d) set which had been left on the spot; besides, the stalks were a little longer. Most of the b) plants flowered too, some had died, but on a whole they made the same impression as those of the a) set.

The c) plants, however, had very few flowers, many had died, and the surviving ones had excessively long stalks, broader leaves and showed no longer the character of a xerophilic plant. They had all grown towards the opening used for airing, which was not the case with those under blue glass.

After these 20 days, the plants were gathered and distilled, the thymol in the oil obtained being determined by transformation into diidothymol.

The oil from a) contained 45 per cent., from b) 36 per cent., from c) 25.5 per cent. and from d) 52.5 per cent. of thymol. As per these results, the formation of thymol seems to decrease as the plant loses its character of a xerophyte. The red rays are most detrimental to the formation of thymol, the blue ones less.

Valerian Oil. According to our own practical experience, dry Thuringian valerian roots yield on distillation 0.5 to 0.9 per cent., those of Dutch origin about 1 per cent.[1]) of essential oil. Swedish valerian root seems to contain a far higher percentage, as Söderberg[2]) reports. He distilled with steam, neutralized the distillate with N/20 lye and shook it with ether. The ether was then distilled off and the residue dried in a desiccator.

The roots (fresh?) collected in spring 1917 from *Valeriana officinalis,* L., contained 2.12 per cent. of volatile oil or, calculated for dry substance, 2.43 per cent., whereas those gathered in autumn of the same year yielded only 1.73 and 2 per cent., respectively.

The rhizomes of *Valeriana sambucifolia,* Mik., dug up in spring 1917, contained 2.82 per cent. of volatile oil, or 3.18 per cent. of the dry substance; those collected in autumn, 2.02 and 2.32 per cent., respectively.

As to the cultivation of valerian, see page 78 of this *Report.*

Wintergreen Oil. Puran Singh[3]) indicates the following constants for an oil distilled at Assam (British India) from *Gaultheria fragrantissima,* Wall. (*G. punctata,* Blume): $d_{16°}$ 1.185, α_D 0, $n_{D25°}$ 1.4000, s. v. (after one hour's saponification) 362.9 = 99.14 per cent. of methyl salicylate[4]), soluble in 6 vols. of alcohol of 70 per cent. Excepting the refraction, which would be too low, the oil comes up to the requirements of the British Pharmacopœia for wintergreen oil. Plants collected in the Nilgiri mountains yielded in winter 0.12 per cent. of oil as calculated for the fresh, and 0.22 per cent. as calculated for the dry material, whereas the Assam material yielded 0.65 per cent.

[1]) Gildemeister and Hoffmann, *Die ätherischen Öle,* 2nd ed., vol. III. page 631. — [2]) *Svensk farm. tidskrift* **1917**, 481; *Schweiz. Apoth. Ztg.* **56** (1918), 161. — [3]) *The Indian Forest Records* **5** (1917), No 8; *Perfum. Record* **8** (1917), 328. — [4]) The s. v. 362.9 means a content of 98.48 per cent. of methyl salicylate, not 99.14 per cent.

from green and 1.2 per cent. from dry leaves. Puran Singh is of opinion that the distillation of wintergreen oil in Assam would pay.

At the time, we found the following constants for an Indian distillate of *Gaultheria punctata,* Blume: $d_{15°}$ 1.1877, α_D inactive, $n_{D20°}$ 1.53485, e. v. 364.8 = 99 per cent. of methyl salicylate, soluble in 7 vols. of alcohol of 70 per cent.[1]).

Regarding the determination of phenol (carbolic acid) in wintergreen oil, see page 64 of this *Report.*

Oil of American Wormseed. In our previous *Report* we mentioned, on page 80, an artificial *Chenopodium* oil, in the concoction of which "art" had gone so far that there was not the slightest resemblance with the composition and efficacity of the genuine oil. A similar product, but styled genuine oil of *Chenopodium,* was sent us for inspection early this year. Its constants were: $d_{15°}$ 0.9534, α_D — 3°, sap. v. 0.9, ester v. 154.0, soluble in 2 vols. of alcohol of 70 per cent. If more alcohol was added, a turbidity occurred which disappeared only with considerable dilution. This oil too did not contain any of the characteristic components of true *Chenopodium* oil, but bodies that do not occur in it at all. Among these was cineole, constituting more than half of the mixture. Furthermore, amyl alcohol was found in it, being present apparently in the form of acetate, which would explain the abnormally high ester value. The smell which, the same as the taste, did not remind in the slightest of wormseed oil, indicated, besides, the presence of anethole and menthol.

It is much to be regretted that such compositions, which have no anthelmintic properties at all, maintain themselves in the market so long.

One of the intestinal parasites of human beings is *Entamœba histolytica,* which up to a short while ago was considered as a special dysentery amœba. Recent investigations, however, have revealed the probability of it being only a degenerated form of *Entamœba tetragena.* In any case, bearers of this parasite must be freed from it because of the danger of spreading dysentery. According to E. L. Walker and W. Emrich[2]), American wormseed oil (*Chenopodium* oil) seems to be suitable for the purpose. A treatment of 14 bearers of *Entamœba* apparently healed 10, the other 4 having relapses when the treatment was over. These relapses may be explained by the fact that the patients had not been given any laxative beforehand, which is absolutely necessary for a complete success. The treatment is as follows: ½ to 1 oz. of magnesium sulphate are given to the patient at 6 a. m.; at 8, 10 and 12 o'clock, 16 minims (1 cc.) of wormseed oil are administered in gelatin capsules, followed at 2 p. m. by 1 oz. of castor oil mixed with 15 minims *(sic!)* of chloroform. These quantities are meant for grown-up people. The dosis of chloroform is very high, being ten times the maximum indicated in the British Pharmacopœia[3]). The wormseed oil used by the authors had been kept for over a year in the tropical heat and light of Central America; freshly distilled oil will most likely act better.

Oil of European Wormseed. How worthless some substitutes are is shown in a publication by R. Wasicky and H. Ortony[4]). The sample investigated by them looked like *Flores cinæ,* containing an admixture of various seeds. It amounted to 36 per cent.,

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[1]) *Report* October 1911, 96. — [2]) *J. Amer. Med. Assoc.* 68 (1917), 1,456; *Pharm. Journ.* 98 (1917), 499. — [3]) The British Pharmacopœia of 1911 indicated 1 to 5 minims. — [4]) *Pharm. Post* 50 (1917).

as the examination showed, of which 17.7 per cent. consisted of the fruits and seeds of *Ornithopus sativus* (serradilla), 10.2 per cent. of soy beans, and the remainder of linseed husks, *Raphanus Raphanistrum* seeds and husks of cereals. On closer investigation, the part corresponding to *Flores cinæ* was found not to be satisfactory either, for it showed all the properties characterizing the santonineless kind of *Cina* described by S. Heyl and O. Tunmann[1]) and Enz[2]). This has a different odour, recalling tansy and noticeable when the drug is rubbed between the fingers. Besides, the small little leaf fragments found in it are covered with woolly hairs, whereas those of the true *Cina* are bald. The microscopical test reveals that phloroglucinol and hydrochloric acid colour the involucral calyx leaves far more intensely red than is the case with those of the true *Cina*. An excellent aid for distinguishing the two species is Reichert's fluorescence microscope[3]). Under the conditions chosen for the test by the authors[4]), it permits of distinguishing between the two at the first glance. The powdered flowerets are observed in concentrated boroglycerin. In the case of true *Cina*, a body is dissolved and emanates from every single particle of the tissue in the shape of a faint, bluish-white comet's tail. The lignified parts of the tissue appear green. With the "santonineless" *Cina* a body is dissolved in a decidedly larger proportion, the "tail" being brilliant and distinctly green. In accordance with the phloroglucinol-hydrochloric-acid test, a farther advanced lignification can be determined through the more considerable occurrence of green-coloured particles of tissue. The authors recommend a more liberal use of ultraviolet rays in microscopic work, being of opinion that the theoretical investigation the same as the applied microscopy will thus be considerably advanced.

In lieu of the missing *Cina*, American wormseed oil *(Oleum chenopodii anthelmintici)* would come into consideration, as far as the stocks go, and then thymol. In retail trade, *Flores Tanaceti*, *Herba Thymi* and perhaps *Herba Chenopodii ambrosioidis* might be supplied as substitutes. They think that after the war it ought to be tried to grow *Chenopodium anthelminticum* in order to become independant of the Russian *Cina* market with the drug thus obtained and the essential oil distilled from it.

Wormwood Oil. As to wormwood growing, see page 80 of this *Report*.

Pharmacopœias.

American Pharmacopœia.

(The Pharmacopœia of the United States of America, 9th decennial revision.)

We mentioned on page 82 of our previous *Report* that on September 1st 1916 the 9th edition of the American Pharmacopœia had come into force. As it reached us too late, we had to put off until now our criticism of the articles concerning our branch of industry.

What we pointed out already when discussing the previous edition of the U. S. Ph. (*Report* April 1906, 69) holds good for the new one as well: there is noticeable every-

[1]) *Apotheker-Ztg.* 28 (1913), 28, 68. — [2]) *Ibidem* 55. — [3]) O. Heimstädt, *Zeitschr. f. wissenschaftl. Mikrosk.* 28 (1911), 330. — [4]) R. Wasicky, *Verh. d. Ges. Deutsch. Naturf. u. Ärzte*, 85. *Vers.*, 1913, I., 534.

where the earnest endeavour to make use of all the progress of science in the tests prescribed. If one has gone too far here and there, *e. g.* as regards the index of refraction for some oils, it is easily understandable and only apt to corroborate our statement. As regards the criterion in question, we are of opinion that it is at least superfluous to introduce it into a pharmacopœia for the examination of essential oils, for on the one hand it is less characteristic for by far most of them than the other constants, whereas on the other the limit values are often so little fixed that they cannot be considered as binding. We shall mention the refraction in the following lines, however, without taking it otherwise into consideration.

It is remarkable that the index of refraction has not been inserted for uniform products, as it there contributes considerably to characterize them and would therefore have been quite in its place. We are going to mention in all such cases the limit values for a temperature of 20°.

The temperature for determining specific gravity, rotation and solubility is 25°, as hitherto, in the first instance referring to water of 25°. The indications concerning the index of refraction are valid for a temperature of 20°.

There are various changes to be recorded with regard to the several articles. *Pinus Pumilio* oil is the only addition, whereas quite a number of oils have been dropped; *viz.*, the oils of copaiba, erigeron, hedeoma, rose and sage, safrole and cinnamaldehyde. *Oleum æthereum* is likewise not mentioned any more in the U. S. Ph.

After these introductory remarks, we now proceed to the discussion of particulars.

Oil of Anise, Oil of Star Anise *(Oleum Anisi).* — Both ordinary anise and Star anise oils are official, but the botanical source must be stated on the label. Colourless or pale yellow; $d_{25°}^{25°}$ 0.978 to 0.988; $\alpha_{D\,25°}$ + 1 to − 2°; $n_{D\,20°}$ 1.544 to 1.560; congenting point not below 15°; soluble in 3 vols. of 90 per cent. alcohol with not more than a slight cloudiness. Tests for neutral reaction, for phenols and heavy metals.

Benzaldehyde *(Benzaldehydum).* — Produced synthetically or obtained from oil of bitter almond and containing not less than 85 per cent. of pare benzaldehyde, assayed by the phenylhydrazine method. Colourless or yellowish; $d_{25°}^{25°}$ about 1.045; slightly soluble in water, miscible with alcohol, ether, or fixed or volatile oils. Tests for absence of hydrocyanic acid, chlorinated products (Beilstein's test), and nitrobenzene.

We miss here a statement concerning the refractive index, which at 20° is between 1.544 and 1.546; compare introduction. It also might have been mentioned that benzaldehyde is optically inactive.

Oil of Bitter Almond *(Oleum Amygdalæ amaræ).* — Yield not less than 85 per cent. of benzaldehyde (phenylhydrazine method). Hydrocyanic acid content, 2 to 4 per cent. Clear, colourless or yellow; $d_{25°}^{25°}$ 1.038 to 1.060[1]); $\alpha_D \pm 0$ or dextrorotatory, not exceeding + 0°10′; $n_{D\,20°}$ 1.5428 to 1.5439; slightly soluble in water, soluble in all proportions in alcohol or ether, as well as in 2 vols. of 70 per cent. alcohol. When first prepared neutral to litmus paper, but developing afterwards acid reaction due to the formation of benzoic acid. Oils showing crystals of this acid must not be dispensed. Tests for absence of heavy metals, chlorinated products, and nitrobenzene.

[1]) We would consider an upper limit of 1.063 more appropriate.

Oil of Cajuput *(Oleum Cajuputi).* — Colourless or yellowish; $d_{25°}^{25°}$ 0.912 to 0.925; α_D not exceeding − 4°; soluble in 1 vol. of 80 per cent. alcohol; test for absence of heavy metals[1]).

[1]) This test, as well as the requirements as to the colour show that the *rectified* oil only is admitted for medicinal use, since the crude oil is green to bluish green owing to the presence of copper.

Camphor *(Camphora).* — White, translucent masses or granules of a tough consistency. M. p. 174 to 177°; $d_{25°}^{25°}$ about 0.990; $[\alpha]_{D25°}$ + 41 to + 42° (in a 10 per cent. solution of alcohol of about 95 per cent. by volume). Slightly soluble in water, freely soluble in alcohol, chloroform, ether, carbon disulphide, petroleum benzine, or in fixed or volatile oils. On gradually heating about 2 gm. of camphor, it sublimes without carbonization and without leaving more than 0.05 per cent. of ash. Tests for absence of moisture (a solution in petroleum benzine [1 + 10] must be clear) and of chlorinated products (Beilstein's test).

Oil of Caraway *(Oleum Cari).* — Colourless or pale yellow; $d_{25°}^{25°}$ 0.900 to 0.910; α_D + 70 to + 80°; soluble in 8 vols. of 80 per cent. alcohol[1]); carvone content, not less than 50 per cent. by volume (sulphite method).

[1]) Oil of caraway is soluble in 2 to 10 vols. of 80 per cent. alcohol.

Oil of Chenopodium *(Oleum Chenopodii).* — Colourless or pale yellowish; $d_{25°}^{25°}$ 0.955 to 0.980[1]); α_D — 4 to — 10°; soluble in 8 vols. of 70 per cent. alcohol[2]).

[1]) The figures give a for the density do not exclude inferior oils; the limits of 0.958 to 0.985 would have been more correct.

[2]) For solution, 3 to 10 vols. of 70 per cent. alcohol are required.

Oil of Cinnamon, rectified *(Oleum Cassiæ).* — Yellowish or brownish, becoming darker and thicker by age and exposure to the air. $d_{25°}^{25°}$ 1.045 to 1.063; α_D + 1 to — 1°; aldehyde content not less than 80 per cent. (sulphite method); tests for absence of heavy metals and of rosin.

Oil of Clove *(Oleum Caryophylli).* — Colourless to pale yellow, becoming darker and thisker by age and exposure to the air. $d_{25°}^{25°}$ 1.38 to 1.060; α_D not exceeding — 1° 10′[1]); soluble in 2 vols. of 70 per cent. alcohol; cugenol content not less than 82 per cent. by volume (assayed with potash solution of 4.5 per cent. strength); when shaking 1 c. c. of the oil with 20 c. c. of hot distilled water, the latter must not show more than a scarcely perceptible acid reaction with litmus. Test for absence of phenol.

[1]) With own distillates, we have observed rotations up to — 1° 35′.

Oil of Coriander *(Oleum Coriandri).* — Colourless or pale yellow; $d_{25°}^{25°}$ 0.863 to 0.875; α_D + 8 to + 13°; soluble in 3 vols. of 70 per cent. alcohol.

Oil of Cubeb *(Oleum Cubebæ).* — Colourless or pale green to yellowish-green[1]); $d_{25°}^{25°}$ 0.905 to 0.925°; α_D — 20 to — 40°[2]); the alcoholic solution is neutral to litmus.

[1]) Its colour is sometimes also bluish-green.

[2]) An upper limit of 43° would be more correct.

Oil of Dwarf Pine *(Oleum Pini Pumilionis).* — Colourless or faintly yellowish; $d_{25°}^{25°}$ 0.863 to 0.869; no portion of the oil must distil below 170°[1]).

[1]) This requirement is too stringent; the initial boiling point required must be 165°, in order to make allowance for the facts.

Eucalyptole *(Eucalyptol).* — Colourless; b. p. 174 to 177°; congealing point: not below 0°; $d_{25°}^{25°}$ 0.921 to 0.923; $\alpha_D \pm 0°$; very slightly soluble in water, miscible with alcohol, chloroform, ether, glacial acetic acid, or fixed or volatile oils; identity reaction with phosphoric acid; tests for absence of saponifiable oils and phenols.

Nothing is stated as to the refractive index, missing also with benzaldehyde; it amounts, at 20°, to 1.454 to 1.459. Compare our introductory remarks.

Oil of Eucalyptus *(Oleum Eucalypti)*. — Colourless or pale yellow[1]); $d_{25°}^{25°}$ 0.905 to 0.925; soluble in 4 vols. of 70 per cent. alcohol; tests for absence of phellandrene. Eucalyptole content, not less than 70 per cent. by volume (per arsenic acid method)[2]).

[1]) The oil has often also a pale greenish colour.

[2]) As to the assay of eucalyptole by means of arsenic acid, compare our *Report* October **1915**, 12.

Eugenol *(Eugenol)*. — Colourless or pale yellow, turning darker and thicker by exposure to the air. B. p. 250 to 255°; $d_{25°}^{25°}$ 1.064 to 1.070; optically inactive and strongly refractive[1]); miscible with alcohol, chloroform, ether, or fixed oils; soluble in twice its volume of 70 per cent. alcohol; identity reaction and test for absence of phenol.

[1]) This statement is of no importance; the refractive index, at 20°, is between 1.539 and 1.542.

Oil of Fennel *(Oleum Fœniculi)*. — Colourless or pale yellow; $d_{25°}^{25°}$ 0.953 to 0.973; α_D + 12 to + 24°; soluble in 8 vols. 80 per cent. alcohol, and in 1 vol. 90 per cent. alcohol, forming a solution neutral to litmus; congealing point not below 3° (cooled down to 0°).

Oil of Juniper *(Oleum Juniperi)*. — Colourless or faintly green or yellow; $d_{25°}^{25°}$ 0.854 to 0.879; $\alpha_D \pm 0°$ to — 15°; soluble in 4 vols. 95 per cent. alcohol with not more than a slight cloudiness.

Oil of Lavender *(Oleum Lavandulæ)*. — Colourless or yellow; $d_{25°}^{25°}$ 0.875 to 0.888; α_D — 1° to — 10°[1]); soluble in 3 vols. 70 per cent. alcohol; tests for absence of alcohol and of glycerin esters.

[1]) The lower limit for the rotation may be — 3°.

Oil of Lemon *(Oleum Limonis)*. — Pale yellow or greenish-yellow; $d_{25°}^{25°}$ 0.851 to 0.855; $\alpha_{D25°}$ + 57 to + 64°[1]); $n_{D20°}$ 1.4744 to 1.4755; α_D of the first 10 per cent. of the distillate not more than 5 degrees less than that of the original oil; n_D of this first 10 per cent. not less than 0.002 nor more than 0.0027 lower than that of the original oil; aldehydes, calculated as citral, not less than 4 per cent. (phenylhydrazine method)[2]).

[1]) The lower limit is still too high and corresponds, at the usual temperature of 20°, to a rotation of 57° 41′; in fact, oils of best quality are frequently met with, whose rotation is as low as 56 to 57° corresponding to a rotation, at 25°, of 55° 20′ to 56° 20′.

[2]) Repeatedly, there has been observed, with otherwise quite faultless lemon oils, a citral content as low as 3.5 per cent. (phenylhydrazine method; compare *Report* April **1914**, 58), so that the figure required above would appear to be too high. Furthermore, there should have been given an upper limit for the citral content, as owing to the requirement above a sophisticator might easily make an inferior oil pass the test by simply adding a few per cent. of citral. The U. S. Ph. should require of a lemon oil an aldehyde content of *about* 4 to 5 per cent., calculated as citral, as determined by the phenylhydrazin method.

Menthol *(Menthol)*. — Colourless, acicular or prismatic crystals; m. p. 42 to 44°; slightly soluble in water, very soluble in alcohol, chloroform, ether, or petroleum benzine; freeby soluble in liquid petrolatum, or fixed or volatile oils; the alcoholic solution is neutral to litmus, and is lævorotatory. On triturating with about an equal weight of camphor, thymol, or hydrated chloral, the mixture becomes liquid. Two grms. menthol, when heated in an open dish on a water bath volatilize without leaving more than 0.05 per cent. of residue; the solution of a few crystals of menthol in 1 c.c. glacial acetic acid, with addition of 3 drops of sulphuric and of 1 drop of nitric acids must not produce a green coloration (thymol).

Methyl salicylate *(Methylis salicylas)*. — The U. S. Ph. comprises under the above title the synthetic product as well as the natural wintergreen oils from *Gaultheria procumbens*, L., and from *Betula lenta*, L. The label must indicate its origin. Colourless,

yellowish, or reddish; b. p. 218 to 221°; $d_{25°}^{25°}$ 1.180 to 1.185 (synthetic oil[1])) or 1.172 to 1.182 (natural oil); $\alpha_D \pm 0°$ (synthetic, or sweet birch oils) or slightly lævorotatory up to $-1°30'$ (gaultheria oil); sparingly soluble in water, miscible with alcohol and glacial acetic acid, soluble in 6 vols. 70 per cent. alcohol[2]) at 25° with not more than a slight cloudiness; the alcoholic solution is neutral or slightly acid to moistened litmus paper. Ester content not less than 98 per cent.; identity reaction with ferric chloride; tests for absence of other volatile oils or petroleum products (1 c. c. ester and 10 c. c. of a 4.5 per cent. potash solution must yield a clear, or slightly cloudy, colourless or faintly yellowish solution without the separation of any oily drops) and of heavy metals[3]).

[1]) The lower limit is too high, it must read 1.177.

[2]) Of 70 per cent. alcohol, 6 to 8 vols. are required for solution.

[3]) The U. S. Ph. test excludes merely the presence of copper and lead, admits, therefore, the iron content frequently observed with wintergreen oil.

Since the synthetic ester is a uniform body, we wish to add its refractive index at 20° : 1.535 to 1.538.

Oil of Mustard, volatile *(Oleum sinapis volatile).* — Both the synthetic and the natural oil are admitted, the label must indicate the origin. Colourless or pale yellow; $d_{25°}^{25°}$ 1.013 to 1.020[1]); $\alpha_D \pm 0°$; b. p. 148 to 154°, the first and last portions of the distillate have nearly the same specific gravity as the original oil. Allyl *iso*thiocyanate content, not less than 92 per cent. (titrimetric method by means of ammoniacal silver nitrate solution according to M. Kuntze [*Arch. der Pharm.* **246** (1908), 58; *Report* April **1908**, 70]); test for absence of phenols.

[1]) The lower limit is far too high and must be lowered down to 1.006. The refraction, also, might have been taken into account, it ranges between 1.527 and 1.531 at 20°.

Oil of Myristica (Nutmeg) *(Oleum Myristicæ).* — Colourless or pale yellow; $d_{25°}^{25°}$ 0.859 to 0.924; α_D + 12 to + 30°[1]); soluble in 3 vols. 90 per cent., or the equal volume of 95 per cent. alcohol. On evaporating 3 gms. of the oil on a water bath, not more than 0.06 gm. residue remains[2]).

[1]) The lower limit is too high; oils distilled by ourselves from best material showed rotations down to + 7°52′. Compare *Report* October **1904**, 65.

[2]) Oil of nutmeg volatilizes comparatively difficultly, so that long heating is necessary, else even good oils yield too high values.

Oil of sweet Orange *(Oleum Aurantii).* — Yellow; $d_{25°}^{25°}$ 0.842 to 0.846; α_{D25} not less than + 94°; $n_{D20°}$ 1.4723 to 1.4737; α_D of the first 10 per cent. is equal to or only slightly greater than that of the original oil[1]); $n_{D20°}$ of these first 10 per cent. not less than 0.0008 nor more than 0.0015 lower than $n_{D20°}$ of the original oil.

[1]) It would be more correct to require that α_D of the first 10 per cent. of the distillate show a rotation equal to or but slightly lower than that of the original oil.

Oil of Peppermint *(Oleum Menthæ piperitæ).* — Colourless; $d_{25°}^{25°}$ 0.896 to 0.908[1]); α_D − 23 to − 33[2]); soluble in 4 vols. 70 per cent. alcohol, showing not more than slight opalescence and no separation of oil globules; ester content (menthyl acetate) not less than 5 per cent.[3]); total menthol not less than 50 per cent.; test for absence of dimethyl sulphide.

[1]) The specific gravity should have more correctly been given as 0.895 to 0.910, corresponding to the values $d_{15°}^{15°}$ 0.900 to 0.915 found with American oils.

[2]) Especially with American oils, rotations down to − 18° have been observed.

[3]) With American oils, the ester content is frequently lower, down to 3 per cent.

Oil of Pimenta *(Oleum Pimentæ).* — Colourless[1]), yellow or reddish, becoming darker with age. $d_{25°}^{25°}$ 1.018 to 1.048; $\alpha_D \pm 0$ to − 4°[2]); soluble in 2 vols. 70 per cent.

alcohol, and in the equal vol. of 90 per cent. alcohol. Eugenol content not less than 65 per cent. by volume (determined with a 4.5 per cent. potash solution).

[1]) We have not yet met with a colourless pimenta oil.

[2]) The rotation of pimenta oil, according to our experience, lies between $-0°40'$ and $-5°$.

Oil of Rosemary *(Oleum Rosmarini).* — Colourless or pale yellow; $d_{25°}^{25°}$ 0.894 to 0.912; soluble in 10 vols. 80 per cent. alcohol; ester content (bornyl acetate) not less than 2.5 per cent.[1]); total borneol not less than 10 per cent.

[1]) The ester content of good oils is often lower, we have observed values as low as 1.2 per cent.

Oil of Santal, East Indian *(Oleum Santali).* — Pale yellow; $d_{25°}^{25°}$ 0.965 to 0.980; α_D $-15°$ to $-20°$; soluble in 5 vols. 70 per cent. alcohol, forming a solution which is slightly acid to litmus. Santalol content not less than 90 per cent.[1]).

[1]) For calculating the santalol content, the U. S. Ph. still sticks to the old formula $C_{15}H_{26}O$, whereas long ago, and recently by Semmler's thorough investigations the formula $C_{15}H_{24}O$ has been established for santalol. The minimum value required above corresponds to a content of 89.2 per cent., calculated for $C_{15}H_{24}O$.

Oil of Sassafras *(Oleum Sassafras).* — Yellow or reddish-yellow; $d_{25°}^{25°}$ 1.065 to 1.077[1]); α_D $+3$ to $+4°$[2]); soluble in 2 vols. 90 per cent. alcohol, the solution is neutral to litmus.

[1]) As lower limit, 1.063 would be more correct.

[2]) With own distillates, we have observed rotations down to $+2°$.

Oil of Spearmint *(Oleum Menthæ viridis).* — Colourless, yellow, or greenish-yellow; $d_{25°}^{25°}$ 0.917 to 0.934[1]); α_D -38 to $-55°$[2]); soluble in 1 vol. 80 per cent. alcohol, forming a clear solution; on further dilution, it usually becomes cloudy; carvone content not less than 43 per cent. by volume (sulphite method).

[1]) The lower limit for the density was given, in the preceding edition of the U. S. Ph., more correctly as 0.914.

[2]) With good American spearmint oils, rotations down to $-34°$ have been observed.

Oil of Star Anise, *vide* Oil of Anise.

Terebene *(Terebenum).* — A liquid consisting of dipentene and other hydrocarbons, obtained by the action of concentrated sulphuric acid on oil of turpentine. Colourless, having a rather agreeable, thyme-like odour, and an aromatic, somewhat terebinthinate taste. B. p. 160 to 172°; $d_{25°}^{25°}$ 0.860 to 0.865; α_D not exceeding $+0°18'$; soluble in 3 vols. 95 per cent. alcohol, slightly soluble in water. Terebene does not redden blue litmus paper moistened with alcohol; on evaporation on a water bath, any residue remaining must not exceed 1 per cent.

Terpin Hydrate *(Terpini Hydras).* — Colourless, lustrous, rhombic prisms, nearly odourless, and having a slightly aromatic and somewhat bitter taste. Heated slowly to about 100° it sublimes in fine needles. When quickly heated, it melts between 115° and 117°, with the less of water. It also loses its water of crystallization slowly over sulphuric acid. One gm. of terpine hydrate dissolves, at 25°, in about 200 c.c. water, in 13 c.c. 95 per cent. alcohol, in 135 c.c. chloroform, and in 140 c.c. ether; also in about 34 c.c. of boiling water, 3 c.c. of boiling alcohol, and in about 1 c.c. of boiling glacial acetic acid. On addition of a few drops of sulphuric acid to a hot aqueous solution of terpin hydrate the liquid becomes turbid and develops a strongly aromatic odour. On incineration of 2 gms., not more than 0.05 per cent. of ash must remain. It has no odour of turpentine, and its saturated, hot aqueous solution is not acid to litmus.

Oil of Thyme *(Oleum Thymi).* — Colourless or red; $d_{25^\circ}^{25^\circ}$ 0.894 to 0.930; α_D slightly lævorotatory; soluble in 2 vols. 80 per cent. alcohol; phenol content not less than 20 per cent. (determined with a 4.5 per cent. soda solution); test for absence of carbolic acid.

Thymol *(Thymol).* — Large, colourless, translucent, rhombic prisus; m. p. 48 to 51°; evaporation residue not exceeding 0.05 per cent.; the alcoholic solution (1 + 20) is optically inactive and neutral to litmus; when triturated with about an equal weight of camphor or menthol, the mixture liquefies; statements as to solubility; identity reactions; test for absence of carbolic acid.

Oil of Turpentine *(Oleum Terebinthinæ).* — Colourless; $d_{25^\circ}^{25^\circ}$ 0.860 to 0.870[1]; α_D variable; soluble in .5 vols. 95 per cent. alcohol; 90 per cent. of the oil boil between 154 and 170°; several tests for absence of mineral oils, etc.

[1]) The lower limit would be fixed more correctly at 0.858.

Oil of Turpentine, rectified *(Oleum Terebinthinæ rectificatum).* — Colourless; $d_{25^\circ}^{25^\circ}$ 0.856 to 0.865[1]); on rapid evaporation on a water bath, 5 c.c. oil leave a residue of not more than 0.015 grm. conforming to the properties and tests for *Oleum Terebinthinæ* (sp. gr. excepted).

[1]) Here also, the lower limit is too high and might be lowered down to 0.853.

Vanillin *(Vanillinum).* — Fine, white, or only very slightly yellowish, crystalline needles. M. p. 80 to 82°; 1 grm. vanillin dissolves in 100 c.c. of water at 25° and in 16 c.c. water of 80°; freely soluble in alcohol, glycerin, chloroform, or ether; the aqueous solution is acid to litmus and is optically inactive; incineration residue not exceeding 0.05 per cent.; identity reaction and test for absence of acetanilide.

Oil of Wintergreen. *Vide* Methyl Salicylate.

Oil of Wormseed, American. *Vide* Oil of Chenopodium.

Chemical Preparations and Drugs.

Almond Oil, sweet. The German Consulate at Beyroot reports on the manufacture of oil from bitter apricot kernels at Damascus[1]). Oils and fats had become very scarce during the war, as olive and sesame oils were used on a large scale as lubricators for the railway and in industrial undertakings. In consequence and owing to the high prices obtainable, a number of small factories were mounted round Damascus with a view to making oil from apricot kernels, which had previously been exported to Europe. The appliances are extremely primitive, consisting of a piece of tree trunk, hollowed out in the shape of a funnel and vertically sunk into the ground. The funnel ends in a tube leading to a receiver holding from 2 to 3 litres. A wooden roller, inserted obliquely into the funnel is then moved round so as to roll along the bowl of the funnel. The lower end of the roller is in the connecting duct between funnel and receiver; the upper, pointed end turns in a hollow of a horizontal wooden beam, which is charged with stones and pulled round by a mule. About 6 or

[1]) *Nachr. f. Hand., Industr. u. Landw.* **1918**, N° 76, p. 4.

8 kilos of shelled apricot kernels are thrown into the funnel and then the apparatus is put into action. The kernels are ground between the roller and the bowl of the funnel, being strongly heated in the process through the friction. After some time, when the kernels form a doughy mass, the oil begins to flow into the receiver. As the process takes about 3 hours, the maximum of oil kernels ground in such an apparatus would not exceed 50 or 60 kilos in 24 hours. The yield amounts to 30 per cent. of oil. Trials to work the kernels like sesame proved successful and afforded 35 per cent.

Almond Powder. That we are living in the times of substitutes, was evidenced by a sample of almond powder, on which our opinion was asked early this year. The product had nothing in common with almond powder, except the name. It contained about 35 per cent. of a silicate, apparently pumice-stone, and otherwise chiefly powdered soy beans, judging by the microscopic aspect.

Ambergris. Whereas there is no longer any doubt regarding the origin of ambergris as a secretion of the sperm-whale, it is unknown as yet in what organ it is formed. Formerly, it was thought that ambergris originated in the bladder, but of late one is more inclined to believe that it is formed in the intestines, as the beaks of cephalopods found in ambergris, which animals constitute, the food of the sperm-whale, are supposed to prove. Th. Zell[1]) explains otherwise the formation of this enigmatic substance. He considers ambergris as a secretion meant to facilitate the meeting of the sexes, such as castoreum and similar highly scented bodies. He points out the fact that the beaver always deposits his secretion at certain places. As sperm-whales, like whales generally, have once lived on land, they will then have taken their ambergris to a definite spot. When they had lost the faculty to go on shore, they went at least near the coast. As all the sperm-whales secrete their ambergris at one definite spot, if possible, it is explicable that quantities of a cwt. are found sometimes, which have got stuck together. Whales having no sense of smell, Zell presumes that they are capable of tasting the ambergris from a great distance.

Zell does not say anything as to how and where ambergris is formed.

The test of ambergris[2]) is a delicate task for the analytical chemist, for the substance is so precious that it is necessary to use it sparingly, which means that the results of the analyses may easily become inaccurate in consequence of dealing with too small quantities. One occasionally meets with indications concerning the examination of this costly aromatic, and J. Lund[3]) recently reported on it. The sample in question came from a sperm-whale killed near New Zealand. It had a feeble aromatic smell, becoming stronger on heating, and at last there was an empyreumatic odour, as from albuminous substances. While being heated, the sample took a dark-brown colour, but the pieces remained soft and fat-like. They went back to their original colour on cooling.

In order to prepare a pure ambergris substance, Lund extracted a piece with ether, when 26 per cent. of an insoluble, light, porous, brownish mass remained, the content of ashes of which amounted to 6 per cent.

The pure ambergris substance, obtained after evaporation of the ether, was a brown, resinous, very sticky mass melting at 52°; however, no special value ought to be attributed

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[1]) *Kosmos, Handweiser für Naturfreunde* **14** (1917), 324. — [2]) Comp. *Report* October **1916**, 68. — [3]) *Tidsskrift for Kemi, Farmaci og Terapi* **1917**, 254; *Apotheker-Ztg.* **33** (1918), 27.

to this figure, as it was impossible to establish accurately the change from the solid into the liquid state. The following constants were found: n_{D50} 1,5028, sap. v. 24, iodine number 78, acetylation number 45. The content of free acids amounted to 3 per cent.

Benzaldehyde. What we said regarding the trade with bitter almond oil (comp. p. 5) holds likewise good for benzaldehyde. Not only that the crude product, containing chlorine is sold as "free from chlorine", but even the highly poisonous nitrobenzene has been supplied instead, as was revealed by samples, recently sent us for examination. Besides, there was a sample which proved to be a 10 to 15 per cent. solution of benzaldehyde in alcohol. Everybody ought to be on the alert, therefore, and have the product tested by competent people, in case he does not feel quite sure.

The qualitative test for chlorine is easy and is conveniently carried out according to the well-known combustion method[1]). However, the quantitative determination presents difficulties sometimes; it is, for instance, made according to Carius. But as M. S. Salamon[2]) correctly remarks, its absorbs too much time and demands a considerable amount of apparatus. He therefore tried other ways recommended and arrived at the following conclusions:—

Piria and Schiff's method, according to which benzaldehyde is heated with lime in a platinum crucible, does not lead to any result, as too much benzaldehyde is lost in the process. But Vaubel's test is quite useful. It consists in heating benzaldehyde with concentrated sulphuric acid and collecting the vapours in silver nitrate solution. The results are satisfactory, especially if a modification indicated by Salamon, is taken advantage of, as follows:—

In a retort, 1 gram of benzaldehyde is mixed with 40 cc. of concentrated sulphuric acid, then 5 cc. of nitric acid are added and the mixture is heated until the vapours conducted into silver nitrate solution do not cause any more a precipitate insoluble in dilute nitric acid. In order to destroy any silver sulphite that may have formed, the silver nitrate solution is boiled after acidulation with dilute nitric acid. The precipitate is treated and weighed in the usual way. The proportions of chlorine found in various samples were:—

according to Vaubel . .	2.14	0.13	1.9	1.7	per cent.
„ „ Carius . .	2.2	0.15	2.0	1.9	„ „

Civet. Occasionally, consular reports refer to the export of civet[3]), for example that of the Aden Consul of the United States[4]), stating that the normal exports from Aden total 45000 $ but that they have decreased since the war broke out. In 1914, about 3½ per cent. of the quantity sold in Aden went to the United States, as compared with 60 per cent. to the value of 21238 $, in 1916. Formerly, France was the chief importer and bought, in addition, from Djibuti. The United States, France, Great Britain and Egypt take up almost the total civet exports from Aden. As far as it is possible to ascertain, the civet sold in Aden comes from the Abessynian highland. The civet cat lives in northern Abessynia, especially in the Shankalla and Malaya districts, where the climate is fairly cool.

Coumarin. In a sample submitted to us for examination, we stated an adulteration that must be considered as an absolute failure, there being an admixture of not less than

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[1]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, page 609. See also *Report* October **1916**, 90. — [2]) *Perfum. Record* 8 (1917), 41. — [3]) Comp. *Report* October **1911**, 111. — [4]) *Chemist and Druggist* **89** (1917), 701.

60 per cent. of sodium sulphate. The adulteration revealed itself at once in that the product could not be converted into ashes completely on a piece of platinum foil and that neither alcohol nor ether dissolved it entirely. When rinsed with ether, the substance left a residue of about 60 per cent., which on closer investigation proved to be sodium sulphate. The cumarin, freed from this admixture, melted already at 65°, instead of at 69 to 70°, so that a further falsification may be suspected. The sample at our disposal being too small, however, nothing definite could be established with regard to this.

We have found the same admixture in heliotropin (see next page).

On page 87 of our *Report* October **1916** we discussed a monograph on coumarins from the pen of H. Simonis. Page 197 of this treatise reads, concerning the hydroxy derivatives of the coumarins, as follows: — It is not to be recommended to term these compound "hydroxycoumarols", on account of possible confusion with the hydroxycoumarones. Preferably, it should be agreed upon to term them unmuistakeably "coumarinols".

This suggestion is opposed by the originator of the above term "hydroxycoumarol", H. Kunz-Krause[1]). The objections raised by Simonis against that denomination are, according to Kunz-Krause, easily refuted by merely alluding to the numerous similarities in the terms especially of organic compounds, *e. g.* benzol—benzone, phenol—phenone, styrol—styrone. Kunz-Krause opposes to Simonis' procedure of substituting his (Kunz-Krause's) terms of a group of bodies by a new name of coumarinols without sound arguments, since firstly there is no conclusive reason for altering the termination, and secondly, coumarin is in the same relation to the coumarols (hydroxycoumarols) as is benzol to the corresponding phenols, *i. e.*, the coumarin molecule is contained in the hydroxycoumarols in so far only, as its H-atoms are not substituted by hydroxy or alkoxy groups. Furthermore, the matter is, says Kunz-Krause, also a question of priority.

Eucalyptole. Since dichloroamine-T (*p*-toluene sulphone dichloroamide) has been used for the treatment of infected wounds[2]), the preparation and purification of this body and of its solvent have grown important. R. B. Krauß and E. Crede[3]), recommend as most suitable solvent a chlorinated eucalyptole of sp. gr. 1.2. For preparing this body the authors conduct, in full day light, chlorine gas into eucalyptole until the sp. gr. amounts to 1.19; they then wash with water, shake with dehydrated sodium carbonate, pour the liquid off and let it stand for one night with fused calcium chloride. After filtering, the oil shows the sp. gr. 1.2 and contains about 31 per cent. chlorine. It dissolves easily 20 per cent. of its own weight of dichloroamine-T. The authors give no statements as to the constitution of the solvent; on prolonged chlorination at 100° or in chloroform solution, a viscid chlorocineole of sp. gr. 1.4 or more is the result. The latter is only a poor solvent for dichloroamine-T, but, according to the authors, it may perhaps be used for other purposes.

A different method for preparing chlorinated eucalyptole is published by Gershenfeld[4]) in a paper entitled, "The Antiseptics and the War", by mixing 500 cc. eucalyptole with 15 g. potassium chlorate and 50 cc. hydrochloric acid ($d\frac{25°}{25°}$ 1.049) and letting the

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[1]) *Pharm. Zentralh.* **58**, (1917), 409. — [2]) Comp. Dakin, Lee, Sweet, Hendricks and Le Conte, *Journ. Amer. med. Assoc.* **69** (1917), 27. — [3]) *Journ. Amer. chem. Soc.* **39** (1917), 2720. — *Amer. Journ. Pharm.* **90** (1918), 16. — [4]) *Amer. Journ. Pharm.* **89** (1917), 487.

mixture stand for 12 hours. The liquid is then washed with water and sodium carbonate solution, anhydrous sodium carbonate is added, and after 24 hours' rest the liquid is filtered off and dried over calcium chloride.

According to former statements published on the action of organomagnesium compounds on intracyclic oxides, it ought to be expected that on treatment of cineole with such bodies an additional compound should be formed. Grignard[1]), for instance, found that cineole, indeed, forms with methylmagnesium iodide an additional compound which reacts extremely violently when heated to 160°. C. F. van Duin[2]) recommends the following working method as being the best. 52 g. cineole are added to a suspension of 56 g. methylmagnesium iodide in ether and after several hours' heating are left to stand for three or four days. The ether is then distilled off and the flask heated up to 160°; the reaction commences and proceeds without external application of heat. The reaction product is fractionated *in vacuo* and the distillate collected up to 85° (21 mm.). By shaking with resorcinol solution, the unattacked cineole is removed and the result is a liquid of the b. p. 170 to 180° (759 mm.) consisting of a mixture of hydrocarbons $C_{10}H_{16}$, from which, however, crystalline derivatives could not be produced. Oxidation with MnO_4K led to acetone and oxalic acid. When using ethylmagnesium bromide, the reaction proceeded less violent and resulted principally in unchanged cineole, in addition to a hydrocarbon $C_{10}H_{16}$. With phenylmagnesium bromide, the reaction proceeded differently; an addition product results also, but it remains unchanged below 200° and yields by further treatment cineole in addition to some diphenyl.

Furthermore, the author has found that cineole cannot be reduced according to Sabatier's method.

Heliotropine. Some samples of heliotropine which were submitted to us for examination from different parts and originated apparently from the same source, were adulterated in a most extraordinary and extense manner. They consisted, namely, to one-half of sodium sulphate! Evidently, the adulterator did not command much skill, since sodium sulphate reveals its presence by its incombustibility as well as by its insolubility in alcohol and ether. Heliotropine being used mostly in alcoholic solution, the consumer will soon notice the sophistication.

When treating the sample with ether on a filter, the sulphate remained insoluble, amounting to 50 to 52 per cent. After evaporating the solvent the residue of heliotropine showed in all cases the correct m. p. of 35 to 36°, thus manifesting that the adulterator had contented himself with this one sophistication.

According to the nature of the solvent used, the action of chlorine or bromine on piperonal (heliotropine) passes off in a different manner. A. M. Bleakly Orr, R. Robinson and M. M. Williams[3]) found that when preparing bromopiperonal by treating piperonal with bromine in acetic acid solution the yield was unsatisfactory, the aldehyde group being partly substituted by bromine. In a neutral solvent, such as carbon disulphide or carbon tetrachloride, the yield of bromo- or of *6*-chloropiperonal is excellent, the formation of by-products being reduced to a minimum; when halogenating, however, in acetic acid solution, *4, 5*-dibromo- or *4, 5*-dichlorocatechol methylene ether result as by-products; m. p. 86° and 82° respectively.

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[1]) *Bull. soc. chim.* III. **29** (1903), 944. — [2]) *Koninkl. Akad. van Wetensch., Amsterdam, Wisk. en Natk. Afd.* **25** (1917), 1366; *Chem. Zentralbl.* **1918**, I. 622. — [3]) *Journ. chem. Soc.* **111** (1917), 946.

Furthermore, the authors describe the preparation of piperonylic acid and of homopiperonylic alcohol by the action of caustic soda on piperonal, by means of adding to a solution of 200 g. sodium hydroxide in 200 c. c. water of 40°, 100 g. piperonal and shaking the mixture vigorously. When than 50 c. c. alcohol were added, the temperature rose quickly. The reaction terminated, water was added in order to dissolve the sodium piperonylate, and the mixture shaken with benzene. On acidulating the aqueous layer, 53 g. piperonylic acid separated. 1.8 g. Piperonal remained unattacked; 32.5 g. homopiperonylic alcohol had been dissolved by the benzene and melted, after recrystallization from light petroleum, at 58°. Fittig and Remsen[1]) give for the alcohol the m. p. 51°; their preparation, however, had been purified by distillation.

We fail to see the reason why the authors give their product the name of "homo"-piperonylic alcohol; Fittig and Remsen term it simply "piperonylic alcohol", this name being, in our opinion, the only correct one.

Amongst the characteristic derivatives of tropin, a product of the cleavage of atropin, the ketone tropinone is found. R. Robinson[2]) has found this product to be easily identified by means of its di-piperonylidene derivative, which is formed on boiling tropinone and piperonal with caustic potash and alcohol, the condensation product separating already during the course of the reaction. From ethyl acetate it crystallizes in bright yellow needles of the m. p. 214° which, when rubbed with sulphuric acid, first show a coppery lustre, yielding afterwards a blue, then a green solution; this changes into yellow on dilution with water. By means of the di-piperonylidene compound even minute traces of tropinone may be identified.

Methyl Salicylate. A. R. Albright[3]) has elaborated a singular test for phenol (carbolic acid), *p*-hydroxybenzoic acid, &c. in artificial oil of wintergreen. It is based on the fact that in a mixture of two bodies of different indices of refraction, the one becomes invisible, in case it is isometrical, if examined under the microscope in a liquid of the same refractive index, whereas the other body then becomes visible. Albright adds to the methyl salicylate, benzoyl chloride in excess, shakes the mixture vigorously and adds dilute potash lye from time to time until the reaction is complete. In this manner the methyl salicylate and all the phenols are transformed into crystalline benzoyl compounds. These are washed with water and recrystallized from hot alcohol, after having previously been dried. He examines the crystals thus obtained in a liquid of the identical refractive index as the benzoyl methyl salicylate (1.658), using as a medium an aqueous solution of mercury potassium iodide of a certain percentage. In this medium, the benzoyl methyl salicylate crystals are invisible in the microscopic field, whereas the other bodies stand out distinctly. Albright thus proved the presence of phenol in genuine and artificial wintergreen oils, as well as in the oil of sweet birch bark. In the artificial product, he found methyl-p-hydroxybenzoate in addition.

Musk. The "Far Eastern Review" of October 1917[4]) contains something on the musk industry in China, which country holds so to speak a monopoly in this domain. About half of the production is consumed in China, principally for making pills, said

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[1]) *Liebig's Annalen* **159** (1871), 138. — [2]) *Journ. chem. Soc.* **111** (1917), 762. — [3]) *Journ. Americ. chem. Soc.* **39** (1917), 820; *Journ. Soc. chem. Industry* **36** (1917), 567. — [4]) *Chemist and Druggist* **110** (1918), 238. — *Americ. Journ. Pharm.* **91** (1918), 194.

to be a specific against cholera. Besides, the Chinese use musk as a remedy against moths and as a perfume. Almost all the Chinese musk comes from Tibet, the chief markets being Sungpan and Tachienlu. Sometimes, when bands of robbers make the road from Sungpan to Chengtu insecure, the musk finds its way into India. This was the case in 1915, when instead of 25367 only 689° ozs. were forwarded. The value of the 1915 production amounted to 266000 $ gold; in 1916, the shipments came up to 2516° ozs. to the value of 407000 $. The chief consumer for musk is France, followed by the United States; in 1915, the order was reversed, the United States buying more than one fourth of the whole output. Small quantities of musk are taken to various places along the Lungngan route, where every coolie seems to have musk and the inns are pervaded by its odour. Musk is adulterated in China more than any other product.

The largest herds of musk deer are found on the southern slope of the Koko-Nor, where the greatest quantities of musk are collected.

There are three kinds in commerce, the best being the Chinese or Tonquin musk, exported chiefly from Shanghai. It is adulterated with dessicated blood, leather chips, small lead balls, peas, &c., so that the pod often only has the smell of the original content. Further, musk is collected in the western Himalayas and exported to India. The commonest kind is the Cabardine or Siberian musk, sent from central Asia into Russia. It is said not to originate from the true musk deer and has an inferior aroma.

The musk deer is spread over a wide part of central Asia, where it prefers the high regions. In summer, it is scarcely ever found below 800 feet of altitude. It mounts as high as the border-line of the birch, rhododendron and juniper bushes, in which it hides in day-time.

Pollantin. One of the plants giving rise to the American autumnal catarrh is the so-called ragweed, *Ambrosia artemisifolia*, L., a composita occurring in Germany too, although only sporadically as an imported plant. It does not come into consideration with us as causing autumnal catarrh. F. W. Heyl[1]) published a provisional analysis of the ambrosia pollen. It came from plants that had been gathered between August 21st and September 2nd. Previous to the investigation, the pollen was deprived of 8.2 per cent. of water by drying it over sulphuric acid. The ambrosia pollen has a diameter of from 0.0095 to 0.02 mm. It was not possible to prove the presence of any starch in the pollen by means of the iodine reaction. 1 gram of pollen consists of about 610 million grains. About 11.83 per cent. of the pollen substance were taken up by dry ether. Hot absolute alcohol dissolved 20.9 per cent. of the pollen previously treated with ether. The substance dissolved in alcohol contained 1.58 per cent. of hydrocarbons, calculated as glucose. There was 0.37 per cent. of phosphorus present in the pollen, 0.03 per cent. of it being soluble in alcohol. The content of nitrogen amounted to 4.99 per cent., 1.08 per cent. being soluble in alcohol. Salt solutions extracted 2.6 per cent. of nitrogen, proteines (0.6 to 0.8 per cent.) as well as basic bodies (1.9 per cent.). A 0.2 per cent. alkali solution deprived the pollen, previously extracted with a salt solution, of 0.8 to 1.1 per cent. of nitrogen; a 1 per cent. sulphuric acid solution then only dissolved a further 0.12 per cent. of nitrogen, whereas the residue still contained 1.2 per cent.

Ambrosia pollen proteine in quantities of 0.000001 to 0.000005 gram produced the ophthalmic reaction with hay-fever patients of average sensitiveness.

[1]) *Journ. Americ. chem. Soc.* **39** (1917), 1470.

W. Scheppegrell[1]) recommends the biological classification of hay-fever pollen. He considers it wrong to make the conjunctival test with a mixed pollen extract and to determine the pollen therapeutics accordingly. There are a good many plants, the pollen of which may produce hay-fever, but the patient is not exposed to them all, and a therapeutics which is directed against such as do not grow in his neighbourhood, is useless. In order to find out what kinds of pollen occur in a district "atmospherical pollen plates" — glass plates with glycerin — should be prepared and exposed. The microscopical examination then generally reveals the preponderence of one kind of pollen, which may be looked upon as the chief cause of the attacks. The presence of 25 pollen grains in a cc. (sq. cm.?) after 24 hours indicates that there is enough pollen in the air to produce attacks of hay-fever in sensitive persons; if there are 100 pollen grains, violent attacks may be supposed. Only pollen carried by the wind produces hay-fever, otherwise only if breathed in. The patient is examined with the pollen occurring in his neighbourhood and the therapeutics then begun according to the reaction. The process is simplified by the fact that the pollen causing hay-fever may be divided into 4 groups according to its chemical and biological effects and that it suffices generally to differentiate in the treatment between these 4 groups. There are only a few plants that are not comprised in them. The investigations have been made for American plants; in Europe almost exclusively gramineæ pollen comes into consideration.

Storax. In 1916, M. Henze[2]) came forth with the surprising news that storax contained considerable quantities of free pimaric and abietinic acids. According to L. van Itallie and H. J. Lemkes[3]), Henze does not seem to have examined any unadulterated storax, for they never succeeded in proving the presence of abietinic and pimaric acids in the pure product.

They attribute but a slight value to the acid and saponification values in judging storax and think that it is more important to determine the contents of cinnamic acid. It is not possible to calculate the contents of free cinnamic acid from the acid value, as then the acids insoluble in water are likewise determined. When boiling with water, varying proportions of the cinnamic acid are dissolved and at the same time some easily saponifiable esters are decomposed. When determining the saponification value, other esters than those of the cinnamic acid seem to come into consideration: hence the differences found in calculating the total cinnamic acid from the saponification value and the bromine titration. The following method is to be recommended for the determination of the content of cinnamic acid: —

1 gram of storax is boiled for an hour with 20 cc. of alcoholic N/2 potash lye under a reflux condenser, the mixture then boiled down on a water bath and the residue dissolved in 25 cc. of water, the aqueous solution shaken with 20 cc. of ether in a separation funnel, after which the aqueous liquid is collected, the ether layer shaken twice with 5 cc. of water each time and the aqueous liquids are united in a vessel holding 1000 cc. One then dilutes with water up to about 950 cc., adds 10 cc. of dilute sulphuric accid, completes the 1000 cc. by adding more water and filtrates. To 100 cc. of the filtrate 10 cc. of N/10 potassium bichromate solution, 1 gram of potassium bromide and 5 cc. of sulphuric acid are added and, after 15 minutes, 1 gram of potassium iodide. After another 5 minutes, one titrates with N/10 thiosulphate solution. Not more than 6.5 cc. thereof ought to be used. Every cc. of potassium bichromate solution corresponds to 7.4 mg. of cinnamic acid.

[1]) *Boston med. and surg. Journ.* **177** (1917), 42; *Therap. Halbmonatsh.* **32** (1918), 106. — [2]) *Berichte* **49** (1916), 1622; *Report* October **1916**, 75. — [3]) *Pharm. Weekblad* **55** (1918), 142; *Apotheker Ztg.* **33** (1918), 110.

Terpine Hydrate. In his discussion of the German Pharmacopœia 5th ed., G. Frerichs[1]) mentions among other things terpine hydrate, regarding the m.p. of which the Pharmacopœia states the following: "Terpine hydrate melts at 116° giving off water, after which the m.p. sinks to 102°". Frerichs says that terpine hydrate melts at 102° only after having been heated long enough to lose all its crystallization water. The m.p. of 116° is only found when heating the terpine hydrate quickly. If the indications of the Pharmacopœia are followed exactly, by heating 1/2 minute for every degree of the ten last degrees, the terpine hydrate loses part of the water already before melting and then melts lower. He therefore proposes to say only: "Terpine hydrate melts, on being heated quickly, at 116° evolving steam bubbles".

Terpineol. Recently, liquid terpineol has been recommended[2]) as reagent in microscopy. H. Sikora[3]) now describes its use for avoiding the shrinking of dry-conserved small preparations, such as gnats and flies. These objects are firstly fixed in van Leeuwen's mixture, with omission of the picric acid, in some cases also of the acetic acid; after some hours they are rinsed carefully in alcohol of 96 per cent., dried thoroughly in absolute alcohol and transferred as slowly as possible, by means of at least five intermediate solutions, into pure terpineol which is to be renewed repeatedly. After prolonged immersion of some days' or even weeks' duration the preparations are dried in open air, which also takes days and weeks. They keep their shape and size even after eight months' conservation without any shrinking.

K. Slawiński[4]) reports on *cis-trans*-isomerism in the terpene series. He treated a solution of terpineol in acetic acid with a 1 per cent. solution of sodium hypochlorite and recrystallized the crystals separating from the reaction mixture after the addition of ether by means of a mixture of light petroleum and acetic ester, and succeeded in isolating two fractions of the m. p. 114° (b. p. 162 to 165° at 15 mm.) and 60 to 80° (b. p. 125 to 155°), respectively. Both bodies revealed themselves as the chlorohydrines of menthane-*1,2,8*-triol. This mixture of chlorohydrines was treated with caustic potash solution of 20 per cent. By extracting the reaction product with ether and with alcohol, a liquid and a crystalline part (m. p. 118 to 118,5°) were isolated. From the liquid portion, distillation yielded small amounts of pinol and pinol hydrate; the author believes the latter to originate solely from the *cis*-chlorohydrin of menthane-*1,2,8*-triol. From the fraction of the b. p. 175 to 180° (13 mm.) there was obtained, by extraction with ether, *cis*-menthane-*1,2,8*-triol. The chlorohydrin of the latter-named body, m. p. 114 to 115°, yielded on treatment with 20 per cent. potash solution, nearly exclusively pinol hydrate. From the mixture of the chlorohydrines (m. p. 60 to 80°), merely a small amount of the menthane-triol (m. p. 116 to 117.5°) could be isolated. Hence, the trihydroxy compound originated from the lower-melting chlorohydrin.

H. J. Prins[5]) demonstrates a simple process of the addition of water to terpineol under the influence of acids. One c.c. of liquid terpineol was shaken in a test-tube with 4 to 5 c.c. of 80 per cent. phosphoric acid at 30°; after short standing the tube is filled with cold water, shaken again and left to stand. After a few minutes, terpin hydrate separates off in crystals. This addition of water may be demonstrated also by aid of sulphuric acid of 60 per cent., but is not so complete as with phosphoric acid.

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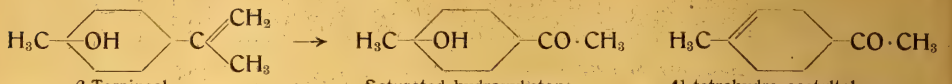
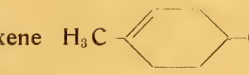
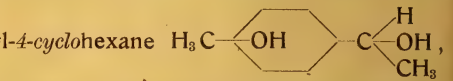
[1]) *Apotheker Ztg.* **32** (1917), 480. — [2]) Comp. *Report* October **1910**, 153. — [3]) *Ztschr. f. wiss. Mikrosk.* **34** (1918), 161; *Chem. Zentralbl.* **1918**, I. 771. — [4]) *Chemik Polski* **15** (1918), 97; *Chem. Zentralbl.* **1918**, I. 920. — [5]) *Chem. Weekblad* **14** (1917), 630.

The chemistry of the alicyclic bodies having been promoted especially by the investigation of the terpineols and terpines, Wallach[1]) directed his interest to a study of the higher and the lower homologues of these unsaturated tertiary alcohols and saturated glycols. Starting from Δ^1-tetrahydro-*p*-acetyltoluene he obtained the lower homologue of terpineol prepared by himself some time ago[2]). Tetrahydro-*p*-acetyltoluene is formed on oxidation of β-terpineol, a saturated hydroxyketone occurring as intermediary product.

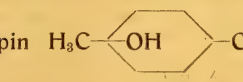


β-Terpineol. Saturated hydroxyketone. Δ^1-tetrahydro-acetyltoluene.

By hydration (shaking with a 4 per cent. sulphuric acid) the unsaturated ketone passed over into the saturated hydroxyketone, which gave a semicarbazone of the m. p. 197 to 198°. Wallach also prepared a dibromide of tetrahydro-*p*-acetyltoluene; m. p. 61°.

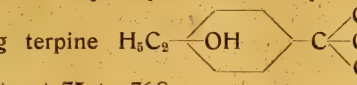
On reducing tetrahydro-*p*-acetyltoluene by means of nascent hydrogen the aforesaid lower homologue of terpineol was obtained, *i. e.*, Δ^1-methyl-*1*-hydroxy-*8*-ethyl-*4*-*cyclo*-hexene  , which on shaking with dilute sulphuric acid passes over into the glycol methyl-*1*-dihydroxy-*1, 8*-ethyl-*4*-*cyclo*hexane  , m. p. 94 to 95°. By means of palladium and hydrogen, Wallach succeeded in transforming the unsaturated alcohol into the saturated body $H_3C-C_6H_{10}-CH(OH)\cdot CH_3$, methyl-*1*-hydroxy-*8*-ethyl-*4*-*cyclo*hexane; b. p. 203 to 205°.

When Δ^1-tetrahydro-*p*-acetyltoluene is brought to react with methyl magnesium iodide, α-terpineol is formed. Since the former body is accessible from β-terpineol, this reaction leads from β-terpineol to the α-isomeride.

On treating Δ^1-tetrahydro-*p*-acetyltoluene with ethyl magnesium iodide, there results a homo-α-terpineol , b. p. 235 to 237°. Its dibromide is an oily liquid; when warming with sodium methoxide solution it yields a homologous pinol which (analogous to the formation of cymene from pinol) very easily passes over into the homologous cymene, *p*-methyl-*sec.*-butyl benzene. Treatment of the homo-α-terpineol with potassium permanganate yields a glycerol $C_{11}H_{19}(OH)_3$; on shaking with dilute sulphuric acid the homo-α-terpineol passes over into a homologous terpin  of the m. p. 65 to 67°. By reducing homo-α-terpineol with palladium and hydrogen, a homologous menthanol , b. p. 223 to 225° (760 mm.) results, whose phenylurethane melts unsharply between 115 and 120° and is evidently a mixture.

Already some time ago Wallach[3]) communicated a method for preparing α-terpineol from nopinone, passing through methyl-nopinol, and also for preparing a homologous

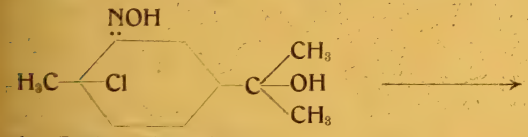
[1]) *Liebig's Annalen* **414** (1917), 204. — [2]) *Ibidem* **324** (1902), 93; *Report* October **1902**, 93. — [3]) *Liebig's Annalen* **360** (1908), 88; *Report* April **1908**, 165.

α-terpineol. The latter alcohol bears the ethyl group in position 1 and is, consequently, isomeric to the aforesaid homoterpineol with the ethyl group in the side-chain. The homoterpineol prepared from ethyl nopinol forms a phenylurethane of the m. p. 92 to 94°. The corresponding terpine  dihydroxy-*1,8*-ethyl-*1*-*iso*propyl-*4*-*cyclo*hexane, melts at 75 to 76°.

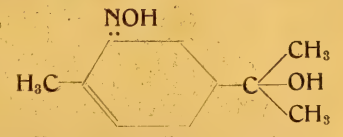
For degrading unsaturated hexacyclic compounds down to benzene hydrocarbons, it was found to be convenient to treat the unsaturated alcohols with one double bond, *i. e.*, the terpineols, with bromine in glacial acetic acid solution, boil the solution until the evolution of hydrogen bromide ceases, and distil the hydrocarbon formed with steam. By this method, benzenic hydrocarbons are rendered accessible which by other means are only difficult to synthesize. From α-terpineol *p*-cymene, from sylveterpineol *m*-cymene[1]), from the afore-described Δ^1-methyl-*1*-hydroxy-*8*-ethyl-*4*-*cyclo*hexene *1,4*-methylethylbenzene may be prepared. Furthermore, Wallach transformed the homo-α-terpineol from Δ^1-tetrahydro-*p*-acetyltoluene *viâ* its bromide into homopinol and the latter, by boiling with sulphuric acid, into *1,4*-methyl*iso*butylbenzene. The homoterpineol from *1,4*-ethylnopinol yielded *1,4*-ethyl*iso*propylbenzene.

Some time ago Wallach[2]) found that nitrosochlorides may be transformed successfully into oximes without any intense heating by making use of the comparatively good solubility in acetone of most nitrosochlorides and by applying pyridine for splitting off hydrogen chloride. By this method, a very satisfactory yield of carvoxime results, when 7 g. limonene nitrosochloride, 3 c. c. pyridine, and 6 c. c. acetone are warmed from 10 to 15 minutes in a boiling water-bath and the clear warm solution treated with some water.

In course of the investigation of the terpineol nitrosochlorides it has been found that the manner in which hydrogen chloride is split off may be markedly influenced according to the reagent used for abstracting the hydrogen chloride. If α-terpineol nitrosochloride (I) is treated in the manner described above for limonene nitrosochloride, with pyridine in acetone solution, the result is an unsaturated oxime of the m. p. 134° (II), formerly termed hydroxy dihydro carvoxime, but more correctly it should be named hydroxy-*8*-carvotanacetone oxime or Δ^6-hydroxy-*8*-menthenone-*2*-oxime. Treatment with sodium acetate, however, leads to an entirely different result. When

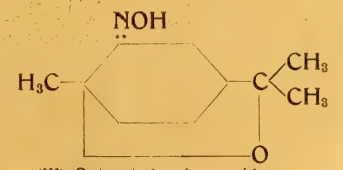


(I) α-Terpineol nitrosochloride.



(II) Δ^6-Hydroxy-*8*-menthenone-*2*-oxime.

triturating α-terpineol nitrosochloride with its own weight of sodium acetate, then adding the five-fold weight of glacial acetic acid and warming until reaction has begun, the chilled mixture yields, after addition of water and after neutralization with alkali, a crystaline



(III) Saturated oxime oxide.

[1]) Haworth, Perkin and Wallach, *Liebig's Annalen* **399** (1913), 166; *Report* October **1913**, 136. — [2]) *Liebig's Annalen* **414** (1918), 258.

product of the m. p. 139°. The latter is saturated and identical with a body obtained some time ago by Cusmano and Linari[1]) also from α-terpineol nitrosochloride, but on a round-about way; it proved to be a saturated oxime oxide (III). Action of mineral acids on this body produced the well-known ketolactone of homoterpenylic acid, m. p. 63°; on oxidation with chromic acid, cineolic acid results from the oxime-oxide.

On a solution of β-terpineol nitrosochloride in acetone, pyridine acts in a more complicated manner. Evidently, there results a non-crystallizing, unsaturated hydroxy oxime. Equally, the interaction of β-terpineol nitrosochloride with alcohols is complicated. In presence of ethyl alcohol, the chlorine atom of the nitrosochloride is apparently exchanged for ethoxyl, thus yielding a rather unstable ethoxyl derivative. With methyl alcohol, β-terpineol nitrosochloride does not produce the corresponding methoxyl compound, but presumably a dihydroxyoxime. On hydrolyzing the various saturated crystalline bodies resulting from the action of alcohols on β-terpineol nitrosochloride, there results in all cases the same body $C_{10}H_{14}O$, a ketone, the semicarbazone of which melts at 218°. The identical ketone is obtained by hydrolizing the unsaturated oxime (resulting by interaction of β-terpineol nitrosochloride with sodium methoxide or with pyridine) by means of sulphuric acid, whereas the oxime, on heating with oxalic acid, produces an aldehyde-like body $C_{10}H_{14}O$, the semicarbazone of which melts at 209°.

Thymol. Evidently, ajowan seed is now used for producing thymol in British India, instead of in Europe, as was the case before the war. We find in an English periodical[2]) the reproduction of a photo, taken in Calcutta, of a 1916 lbs. lot of thymol, intended for New York and London.

On former occasions, we have pointed out that nothing had transpired, so far, as to the properties of the thymol produced in England or British India; in fact, not so very long ago the English had not yet succeeded in this simple manufacture, for the product obtained did not come up to the requirements of the British Pharmacopœia.

As to the possibility of obtaining thymol from the oil of *Ocimum viride*, see p. 36 of this *Report*.

According to H. Elion[3]), the method for determining thymol, salicylates and similar bodies, described as new by A. Seidell[4]), and according to which the absorption of bromine is measured, was known long ago and published by him in 1888[5]).

G. A. Prins[6]) calls attention to the poisonous action of thymol. It generally passes as inoffensive, however, Leichtenstein witnessed a fatal case of poisoning after the administration of 6 grams of thymol. In other cases, less severe symptoms of poisoning, vomiting, stomach-ache, colic, etc. were observed after taking big doses[7]). Thymol being used in quantities of 0.5 to 1.5 g. daily, caution is advisable. It should be remembered that thymol is contained in numerous dentifrices as well as in various modern remedies, such as Pyrenol, Archovin, Pertussin, Thymipin, Thymobromal, Thymoform and Aristol.

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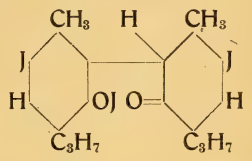
[1]) *Chem. Zentralbl.* **1912**, I. 1012; *Report* October **1912**, 167. — [2]) *Chemist and Druggist* **90** (1918), 48. — [3]) *Journ. American chem. Soc.* **39** (1917), 1513. — [4]) *American chem. Journ.* **47** (1912), 508; *Report* October **1912**, 134. — [5]) *Recueil trav. chim. of the P.-B.* II. **7** (1888), 211. — [6]) *Ned. Tijdschr. v. Geneesk.* **1917**, 2057; *Pharm. Weekblad.* — According to *Apotheker Ztg.* **33** (1918), 132. — [7]) There are no indications as to the size of the doses.

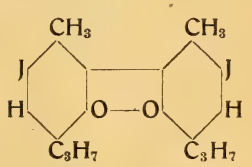
Some time ago, P. Lavialle and A. Aubry[1]) have pointed out that the use of thymol, which in itself has a strongly hæmolytical action, as a preservative especially for vegetable extracts, has often led to erroneous assertions in that the hæmolytical action of the thymol has been described as a property of the substance under investigation. The same applies to the surface tension of urine to which thymol had been added. Derrien and Colombier[2]), who have gone more closely into the matter and have studied the drawbacks of the various substances recommended for the preservation of urine, call attention to the fact that urine preserved with thymol shows a reduction of the surface tension, whereas Hays reaction[3]) then always gives a positive result. Said reaction must therefore be applied cautiously if the urine tested has been preserved with thymol. Camphor exercises the same disturbing influence, although in a lesser degree.

On page 101 of our *Report* of October **1917**, we mentioned a communication of H. P. Goodrich[4]), who recommends a saturated aqueous thymol solution as a dentifrice. According to J. T. Hall[5]), thymol is not at all appropriate for the purpose, as it acts far too strongly and has an injurious effect upon the gums, if used for any length of time. For that reason, Goodrich now recommends to dilute the thymol solution, especially during the warm part of the year.

By action of iodine on thymol, there results a body termed "aristol", regarded as a derivation of dimolecular thymol[6]). The discoverers, Messinger and Vortmann[7]), expressed themselves as to the structure of aristol only with reserve. By acting with iodine and potassium iodide on an alkaline solution of thymol, a red iodothymol is formed, which on heating, or keeping in the dry state, splits off part of its iodine and passes over into a pale yellow, equally iodinated body. The red iodothymol was taken by Messinger and Vortmann to be a iodinated derivative of a thymol ester of hypoiodous acid of the formula:—



This theory, according to J. Bougault[8]), does not agree with the facts. On saponification, for instance, aristol does not yield hypoiodous acid; experimental details, however, are not published. Bougault believes aristol to be a doubly iodinated quinone derivative of a dimolecular thymol, possibly of the formula:—



In Bougault's opinion, there exists only *one* aristol, the yellow preparation; the red body being the yellow product coloured by free iodine and easily splitting off iodine. He regarded aristol as a stable body, the assumption that its therapeutical value is based on the easy liberation of iodine, being erroneous, the action depending merely on its antiseptic properties.

Tolu Balsam. A publication of G. C. van Walsem[9]) refers to embedding materials of a higher refractive power, especially balsam of tolu. It had been observed that preparations kept in Canada balsam lost considerably in comparison with the preliminary examination in oil of cloves. The cause was found to be that the Canada

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[1]) *Bull. Sciences pharmacol.* **23** (1916), 193, 266; *Report* October **1917**, 105. — [2]) *Bull. Soc. chim.* IV. **21** (1917), 133. — [3]) Sprinkling flowers of sulphur on the urine; the sulphur sinks to the bottom if bile acids are present. — [4]) *British medical Journ.* **1917**, I. 473; *Chemist and Druggist* **89** (1917), 376. — [5]) *British medical Journ.* **1917**, II. 99; *Chemist and Druggist* **89** (1917), 783. — [6]) Comp. *Bericht* April **1890**, 54. — [7]) *Berichte* **22** (1889), 2316. — [8]) *Journ. de Pharm. et Chim.* VII. **17** (1918), 221. — [9]) *Zeitschr. f. wiss. Mikrosk.* **34** (1918), 154; *Chem. Zentralbl.* **1918**, I. 771.

balsam used had not the refractive index $n_D = 1.535$, *i. e.* very near that of oil of cloves (1.533), but $n_{D16.6^0}$ 1.517. This drawback was removed by using balsam of tolu, which had so far come into consideration only for the investigation of *diatomaceæ*, when all the details stood out very distinctly. Van Walsem uses a solution prepared by allowing a mixture of 10 grams of powdered balsam of tolu and 10 cc. of chloroform to stand over night and then decanting it.

Vanillin. In a treatise on vanillin and its adulteration, G. Issoglio[1]) recommends proceeding as follows in order to prove the presence of salicylic acid: 20 grams of vanillin are dissolved in ether and then twice shaken for 1/4 hour with 100 cc., each time, of a mixture of equal parts of water and saturated sodium bisulphite solution. The aqueous solutions are shaken with a little ether and the ethereal solutions put together. Then, the aqueous solutions are acidulated with dilute sulphuric acid, the sulphur dioxide is removed by introducing hydrogen and the vanillin shaken out with ether. The first ethereal solution contains the salicylic acid. One washes it with water, concentrates strongly and allows to crystallize over sulphuric acid.

In order to detect acetanilide in vanillin, he shakes the ethereal solution with 10 per cent. spirits of ammonia until it is no longer coloured yellow. The acetanilide passes over into the ether, traces remaining in the spirits of ammonia. He acidulates, shakes with ether, dissolves the residue of evaporation in highly diluted spirits of ammonia and shakes again with ether.

He determines benzoic acid by extracting vanillin in the cold with very dilute spirits of ammonia, filtrates, evaporates, dissolves in water and treats with ether. The presence of benzoic acid in the aqueous liquid can be proved with the aid of ferric chloride.

We have, at the time, detected salicylic acid in vanillin by shaking the ethereal solution with a saturated sodium bicarbonate solution[2]).

M. Bamberger and H. von Klimburg[3]) proved the presence of vanillin in the resinous deposits formed over scars by *Pinus Cembra*, L., *Pinaceæ*. The crude resin had an agreeable aromatic odour, recalling that of vanillin and, perhaps, at the same time somewhat that of free butyric acid. The latter was more noticeable with the powdered resin. The vanillin was contained in the aqueous extract of the resin and its presence was proved by the red colour produced with phloroglucin and hydrochloric acid.

By the way, vanillin has been found repeatedly in various resins.

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[1]) *Giorn. Farm. Chim.* **66** (1917), 121; *Chem. Zentralbl.* **1917**, II. 495. — [2]) *Report* April 1915, 59. — [3]) *Monatsh. f. Chem.* 38 (1917), 462.

Notes on Scientific Research in the Domain of the Terpenes and Essential oils.

General.

"The Germans in the Provence, the Germans and our Cypress Trees" is the title of an article published by M. Provence in *"Le Feu"* (1917, pages 114 to 120). It is quite characteristic of the tacties of journalistic warfare. A. Binz[1]) turns against Provence's false assertions and publishes a translation of the article, omitting only some unimportant passages. An extract therefrom will be given in the following lines.

"After a historial introduction, Provence talks about cypress oil and its use, mentioning that the Romans availed themselves of a decoction of the fruits against dysentery. In the Middle Ages, they were used as a remedy against scrofula. A physician in Aix in the Provence prepares from them a remedy against piles. But the most important proceeding founded on the elaboration of the cypress tree and which induced the distillers Schimmel to seek it in the Provence, is the treatment of whooping cough. A romanic scientist, Dr. J. M. Bravo, who published the results of his discovery in the *Revista Medicale de Chile,* found in 1890 cypress oil to be an excellent remedy against this illness. We shall revert more fully to the Chilian doctor's work and to Schimmel's industrial pillage based upon it".

Binz continues: "A description of cypress oil follows, which we can here pass in silence, and the reader now expects the disclosure of Schimmel's misdeeds, which, however, shrinks to the following harmless statement:—

"In 1890, Dr. Bravo proposed in the above named Chilian periodical the use of cypress oil as a specific against whooping cough. The cypress tree is widely spread in his country. In 1892, the *"Deutsche Medizinalzeitung"* recommended cypress oil for treating whooping cough. Since then, our *"Boches"* have appropriated the discovery of the *"savant latin"*, have given it a German name (!) and tried to industrialize it through Schimmels in order to make it a source of profit for the country. Since 1894, the Miltitz distillers produced the oil on a large scale. Physicians like Prof. Dr. Soltmann, Dr. H. . . ., of Friedenau, and Dr. Winterseel spread the use of the product, which we owe to the discovery of the Chilian doctor".

As Binz further explains, Provence then discusses in detail the publications of said German physicians or, to speak in his own terms, of these *"expérimentateurs boches"*, and at the same time describes quite correctly, following Schimmel's *Reports,* what progress the production of cypress oil has made in furtherance of medicine. The way in which it is done, however, is meant to give the impression that Schimmels were no better than robbers:—

"Les abatteurs de cyprès étaient des misérables, que l'opinion unanime reprouvait".

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[1]) *Deutsche Parf. Ztg.* 4 (1918), 19.

Binz quite correctly replies:—

"Let us state in the first place that in Gildemeister's well-known book *"The Volatile Oils"*, publised by Schimmel & Co., Bravo's scientific priority is recognized with all desirable clearness, for it is there mentioned (vol. I, page 98 of the 2nd ed.) that the above-named recommended cypress oil, in 1892, as a remedy against whooping cough. If Provence therefore says that Schimmels "pillaged Bravo's work", it is a lie. Besides, the obvious answer to Provence's abusive pamphlet is, that nobody can be reproved for opening up the natural resources of a country for the common good. An industry based upon it is not only licit, but constitutes a merit on behalf of humanity, especially if it is a question of supplying it with a new remedy, as is here the case. Should really a landscape suffer from it, it would be less important than the therapeutical aim and, besides, this would concern only the relative authorities. A possible reproach could only have been directed against the industrials in the country, who apparently were lacking in activity, whereas the *"Boches"* showed it much to Mr. Provence's grief. He feels this well enough and contradicts himself by continuing as follows:—

"As is to be seen, cypress oil is a source of considerable revenues. The firm of Schimmel never denied it. But now the utilization will steadily increase. It is true, France uses the oil but little against whooping cough, but Germany and the United States to a very great extent. They did not get it from Chile, but from the Provence through Schimmel. It was mentioned before that the United States are the best customers for lavender oil from the Provence. Would it not be possible, now they are our allies, to come to an agreement to the effect that France supplies them with lavender oil exclusively and in part with cypress oil, without awaiting the amiable return of the Germans?

Our campaign has no other object but to nationalize the undertakings in our Provence and to eject all elements of the *"Boches"* type as well as other undesirable aliens. Through a cordial agreement among the producers, the oils extracted from our plants might signify a source of considerable income.

I said before what cypress oil is used for in the United States and elsewhere, but there are other ways of using it too. In these last years emphysemas have been treated with cypress oil, and its employment in this direction will soon spread.

The Provence possesses there again a lucrative mine; now, that Schimmels are removed, the question is to take matters in hand, to supply direct the best consumers, the United States, but not to uproot the trees, as Schimmels did. For he was in a hurry, he, the spy, knew that the war was approaching and did not think of the future. We must foster the cultivation of the tree and only cut the parts required. Let us do it before the Leipzig people return or perhaps the Norwegians come in order to appropriate these riches, as they did at the time with the bauxite, supported by the greed of the land-owners, the lazy indifference of the capitalists and the unfriendly stupidity of the neighbouring poor. Let us plant cypress trees again. It is the duty of every inhabitant of the Provence. They ought to plant them with the firm oath never to let them be carried away by the bloodstained hands of Leipzig distillers".

Binz replies:—

"Mr. Provence does not seem to realize that the "bloodstained Leipzig distillers" would not have invested such large sums in a factory plant in southern France, if they had foreseen a war or helped to prepare it by spying. Absolutely devoid of common sense is the reproach that Schimmels uprooted the trees. In case such destructive work should have been done, Schimmels could not be blamed, but those who sold them the cypress branches. They were in the main the public administrators of forests and, in addition, perhaps some private people, but this cannot now be stated with certainty.

But as the material was paid by the weight, the buyers will certainly have taken care to receive only branches and no trunks which yield little oil. Mr. Provence's whole article is therefore due to ignorance or constitutes a vile calumny.

Already before the war, it had been necessary, in Germany, to parry Provence's libels and in the article here translated this literary feud is continued in a form that might be amusing, if it did not represent a symptom of instigation, with which our enemies tarnish the century".

Binz then quotes the relative passage from our *Report* of April 1913, which we beg to copy here for the sake of completeness:—

"An article by one Marcel Provence, entitled *"Les Allemands en Provence"*, appeared last October in *"Les Quatre-Dauphins"*, a monthly review, and was reprinted in several local papers in the South of France. Its object apparently was to stir up animosity against our works at Barrême among the population of the lavender districts. We would take no notice here of this attack, which is thoroughly characteristic of the tactics of the French chauvinist press, were it not that we cannot bring ourselves to deprive our readers altogether of this comic contribution — for as such every normally constituted person, no matter what may be his nationality, will regard it. The author depicts what he saw on the occasion of a visit which (without permission, by the way) he paid to our factory at Barrême. He grows excited because the greater part of the installation came from Germany. But the special object which provoked his indignation was a harmless ornament in the gable of the building, which owes its existence to the fancy of our French architect, but in which this patriotic writer espies the likeness of a German soldier's peaked helmet! But even this is not enough. The fact that our peaceful little factory is only 25 metres distant from the railway should, he thinks, afford grave cause of misgiving, for "strategic reasons". It is therefore obvious that we are believed to contemplate a military attack upon the little "back-block" line from Puget-Théniers to Digne! The article in qestion brims over with these and similar horrors! We have been much amused by it, especially because we have heard that it was inspired by one of our competitors in the South of France. But how poor an opinion must an author have of the intelligence of his readers that he should dare to dish up such rubbish to them! Fortunately we have a better opinion of the people of Barrême, to whom the establishment of our works has brought nothing but advantage, and we know how they look upon such libels. Mr. Marcel Provence might have spared himself this public exposure!"

Provence replies to this in *"Le Feu"*:—

"How a French author was treated by German spies before the war: —

I found in the library of the *École de Pharmacie de Paris* the famous *Report* of April 1913, in which Schimmels offend me. I translate the passage referring to me, but I esteem my readers too highly as to render a certain baseness. I therefore omit one sentence. Here is the wording in all its beauty."

In rectifying his defence[1]) Binz says to this among other things: —

"The *"bassesse"* of Schimmel's *Report* is the following passage of the German original, where it reads regarding the attacks in the press: "We hear that one of our competitors in the South of France is supposed to be the instigator".

Provence deemed it advisable to suppress these words, "out of esteem for his readers", as he pretends. This threadbare argumentation will not deceive anybody. The real cause was another: Schimmel's above quoted sentence, however mildly expressed, bears more than the stamp of probability, for since then it has come home

[1]) *Deutsche Parf.-Ztg.* 4 (1918), 31.

to the people at large, how systematically the French and quite especially also the British Press, since many, many years, long before the war already, have tried to shake the German trade abroad. It may therefore be assumed with certainty that similar forces, nourished with jealousy, had been at work also in Barrême, so that Schimmel's *Report* exposes that evil turn of our enemies' mind, of which they have most to be ashamed of: the envy of the successes of Germany's industry and commerce, the *Propter Invidiam* of Tacitus, this shameful main cause of the war, which our enemies try in vain to hide behind their phrases of the fight for right and for the freedom of the small nations. That is what the afore said passage in Schimmel's *Report* stigmatizes. A remainder of sense of shame has induced Provence to be silent on the subject."

In addition to this, we beg to discuss another article by Binz[1]), called *"Stimmen aus Frankreich"* (Voices from France), in which he calls attention to some remarks in the French press, which are of interest for our industry.

E. Hugues writes in *"L'industrie chimique"* of 1st September 1917 under the heading *"La Parfumerie"*: —

"In and round Grasse, transactions to the value of 20 million francs per year were made before August 1914, of which about half concerns the proper flower district. Ten millions therefore are the share of the plain and represent the value of jessamine, tuberoses, cassie, orange, rose-flowers and others which alternately were picked by the light hands of the female gatherers.

Did the figure of 20 millions decrease since the declaration of war? We can reply with no. Did it increase? A little, perhaps, necessarily. The period of stagnation, caused by the first surprise, was followed by a time of unusual activity. The exports were as large, if not larger, to the countries left open by the law and still more by conscience, *i. e.* American States. The transactions with Germany before the war were really very considerable, and it was to be supposed that the war would reduce the figure of 20 millions. But, quite on the contrary, an increase is to be booked. The explanation is to be found in that we have taken over part of Germany's former exports.

The salient point for our sphere of action, for France, for the industry at large, is that a competition has begun, the continuation of which is possible if everything be well organized for the purpose. We admit that the assertion, Germany's exports ceased with the outbreak of hostilities, borders on folly, for goods have frequently been sent from there on round-about ways. But they are handicapped. We have availed ourselves thereof and are in a position to follow up this advantage. Already on a small scale, union can do a good deal, how much more in a wider sense, and it would be almighty, favoured by the present events, if it took the shape of an interallied league.

Here as everywhere, or perhaps more than anywhere else, the German has done mean underhand work, by undermining everything and spreading unrest and confusion.

To the sun, to the climate that bade him stop, he replied: "be it so", but inwardly he smiled mockingly, saying to himself: "I shall organize to my advantage".

Who does not know that monthly review, which was chosen as a kind of breviary, the greater the pity, as it was full of incomprehensible formulæ with names several decimetres long!

Less science, hang it! Is it not perhaps the licorice meant to sweeten the pill? The public at large, the sincere and confident buyers, do they want these angular figures, these kites with which the German darkened the sky of his illoyal business manœuvres?"

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[1]) *Deutsche Parf.-Ztg.* 4 (1918), 65, 83.

Thus far Hugues' article. What he then says about perfumery and essential oils, is of less interest for us. We only do not wish to keep from our readers what he communicates regarding the imports from French colonies.

"The metropole and our colonies supply almost everything we want and there is no need for us to be obliged to pay tribute to others.

Why had most things to come from Hamburg? Are we lacking means to bring them to Havre or Marseilles? What was amiss? What was amiss in order to protect our interests better?"

Binz says quite to the point that the most striking feature in the article is the repulse of German scientific publications — apparently Schimmel's *Reports* — and, at the same time, the reluctant acknowledgement of their value and of the German chemical achievements, by indicating how they can be imitated. It is not conceit if we say: *Germania præceptor mundi.* We must be satisfied, however, with having reaped bitter enmity for it instead of thanks.

Binz then discusses an article of M. Ajam in *"L'exportateur français"* of 27. 12. 17 entitled: *"Une industrie bien française. La Parfumerie".* According to it, France's exports of perfumery are worth from 50 to 60 million Francs in gold per year. As the statistics show, the French manufacture rose from 12 million Francs, in 1836, to 100 million Francs, in 1912. The United States are good customers for French scents; it is true, the Americans have tried to cultivate flowers in California, but without any great success, owing to the high cost of hand labour. In spite of a protective duty of 25 per cent. of the value, which is the minimum rate, the American perfumers have not been able to prevent a considerable invasion of French products. Nearly the same applies to all the other countries, except Japan, where the activity and spirit of enterprise of the people have made the perfume manufacture develop rapidly, so that it threatens France with serious competition, especially in China.

Above all, Ajam lays stress on the necessity of training chemists in order to enable France to maintain its prestige as perfume manufacturer after the war.

In the same number of the *"Exportateur,"* there is an editorial note: "How to protect the interests of the perfumery trade". It is stated therein that the germanophile tendencies in Scandinavia and Holland have induced the Government to stop all exports to those countries, as it was to be feared that the goods would be forwarded at once to Germany or her allies.

This measure, although excellent in principle, missed its aim, Ajam thinks, for a differentiation ought to have been made regarding articles unsuitable for military use, such as products of the perfumery and allied industries, the exports of which are a source of France's wealth. The Germans are the first amongst the competitors who gained a firm footing.

At another place[1]), Binz discusses an article by M. Provence, published in *"Le Feu"* of 15. 11. 17, in which he gets excited about Professor Haller's nomination as honorary president of the New Society for Chemical Industry in Paris, for "Professor Haller wrote the propaganda preface for Schimmel, he is the author of the preface and the notes in the book on essential oils, published by Schimmel in Leipzig", etc., etc. Furthermore, Provence has to say the following about Professor Haller:—

"Camphor consignments of the firm of Schimmel were seized by the Neuilly Customs-house.

The best expert for them was their propaganda preface writer Haller. Those people with peaked helmet coats of arms at their Barrême factory wrote: 'Mr. Haller, professor

[1]) *Deutsche Parf.-Ztg.* **4** (1918), 82.

at the Sorbonne, has done such important work with regard to camphor, that nobody can be more competent on the subject than he'.

Schimmels meant to make the camphor pass as something else."

Provence cannot grasp that as honorary president a man could have been chosen, who served the *Boches*, those poisoners from Leipzig, those distillers from Bodenbach on the Elbe and Barrême.

Although we attach but little value to Mr. Provence's arguments, we have copied them here in order to show our readers the tone of certain French chauvinistic papers and what the public there will accept.

Cultivation of medicinal plants. — The endeavour to make us independant of foreign countries with regard to the supply of medicinal plants has called forth the publication of numerous articles on such plants and the foundation of the periodical *"Heil- und Gewürzpflanzen"* (medicinal and spice plants)[1]). We here submit an extract of an article by H. Geiger[2]), which appeared in said monthly paper: —

One either collects young wild plants of valerian *(Valeriana officinalis,* L., *Valerianaceæ)* and plants them about one foot apart on a field, or one gets young plants from seeds during the summer and sets them on a field in the following spring. As valerian seeds are very small, they must be strewn on garden beds and pressed down with a flat piece of wood or with a spade. These seed-beds ought to be sprayed, not watered in the ordinary way. The field ought to be fertile and situated in the neighbourhood of water. Valerian demands but little care; hoeing it once will do. The plants may be dug up already in October of the first year.

Angelica *(Archangelica officinalis,* Hoffm., *Umbelliferæ)* is propagated by means of seeds. Geiger recommends making little furrows with a hoe, in autumn, about 30 to 40 cm. apart and to sow very sparsely with the hand or to drill the seeds. One then rakes and harrows. In April of the next year, the young plants become visible and, aided by repeated hoeing, grow fairly quickly and can be dug out with a spade, in autumn. The strongly interlaced plants are separated and, after the leaves have been removed, planted out on stubble-fields, manured with stable-dung, 50 cm. apart in every direction. In order to protect them against frost, they are often covered with long straw. Geiger recommends to harrow or loosen the soil with a hoe, in the following spring, before the young shoots have come through, and to strew 1 cwt. of superphosphate of ammonia (9 : 9) per every 5000 sq.m., to repeat hoeing several times and to weed at least once, in May. Weeding is not necessary any more, as soon as the plants have developed sufficiently to cover the ground, thus keeping down the weeds. Careful growers remove the flower-bud at an early stage, so that all the nourishment goes into the roots.

Angelica must not be grown on soil freshly manured, as the plants then suffer from hair-worms. When setting the young plants, they must be examined and those already attacked, removed.

The seeds of the common chamomile *(Matricaria Chamomilla,* L., *Compositæ)* are strewn sparsely by hand on beds 1.4 m. wide, pressed down a little with a spade and sprayed carefully; weeding is not necessary.

Lovage *(Levisticum officinale,* Koch, *Umbelliferæ)* is sown in November/December, or, as it is sensitive to frost, in March, on stubble-fields manured with stable dung. For every 5000 sq. m., about 2 kg. of seed are required. The first year, the plants are

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[1]) Comp. *Report* October **1917**, 110. — [2]) *Heil- und Gewürzpflanzen* **1** (1917), 33, 68, 102.

treated just like angelica, only that they need not be farther apart from each other than 40 cm. in every direction. The second year, the plants must be covered with long straw, in winter, so as to protect them against frost. Lovage thrives even in exposed places, but requires good soil.

Balm-mint *(Melissa officinalis,* L., *Labiatæ)* is propagated by dividing the plants. Only if it is a question of creating fresh plantations, the seeds are sown in April and the young plants put out on a field in the following spring, 40 cm. apart all round. Already in the second year, a bushy plant will develop, about 30 cm. high. Balm-mint is sensitive to frost, as may be deducted from the yellow colour of the leaves, when the temperature has been low. It thrives in fairly high and exposed places, if there are no unforeseen unfavourable climatic influences. Misty valleys are to be avoided. The planting space need not exceed 30 cm., when balm-mint growing will be all the more remunerative. Hoeing after the first and second cuttings seems to foster the growth. The better the soil, the more favourable it is for growing balm-mint.

Geiger likewise describes the cultivation of peppermint *(Mentha piperita,* L., *Labiatæ).* Although it is certainly more generally known, we mean to copy here the chief points, in view of the keen interest shown everywhere for growing medicinal plants. Peppermint is propagated by dividing the plants. In autumn, after the last cutting, the old peppermint fields are ploughed about 20 cm. deep and the torn suckers are planted, 10 cm. apart, on a well-prepared field, preferably one that has borne potatoes, turnips or cabbage. The preparation includes manuring with stable-dung. The field is ploughed in the usual rows, the fresh (white) parts of the root-stocks are put into the furrows and trodden in with bare feet. The plough then covers them again. Afterwards, a light harrow is passed over the field. The planting material, transported in baskets or carts, must be sprayed in warm weather, so as to prevent its getting dry. During the night, it is advisable to cover it with soil. The suckers will root still in the same autumn. Next spring, the destruction of the weeds must set in early. Manuring with about 1 cwt. of superphosphate of ammonia (9 : 9) will pay well. The chief item for success is a well-prepared soil, not too dry and, as far as possible, free from weeds. Thorough weeding, soon after the plants have begun to sprout and after the first and second cuttings, is necessary. During the crops, the plants can be multiplied through putting the tips of the strongest shoots in frames. This promises great success and the number of plants can be increased twentyfold, without there being any noticeable lessening of the crop. To this effect, the tips of the most vigourous shoots, with the uppermost pair of leaves, are cut off slantingly just above the second leaf-pair and planted in frames with the aid of a dibble. A frame of 1 : 1.2 m. holds about 400 such slips. The frames are kept shut for a week and sprayed twice daily. In order to protect the slips against scorching, the frame-windows should be strewn with soil. As soon as the slips have rooted, the frames can be aired little by little. By taking off the tips, the slips are induced to grow in bredth, so that, four weeks after having been planted, they form a real carpet. A fortnight after, they can be used already for filling up gaps in the old fields or starting fresh ones. It is of advantage to cover the fields with good, moist humus after the weeding. The roots which have been laid bare are thus covered and the growth even of weakly plants is thereby greatly enhanced. Peppermint thrives on formerly moory soil with clay subsoil, which provides the necessary moisture.

From sage *(Salvia officinalis,* L., *Labiatæ),* slips can be taken or old plants can be divided, in autumn, and set in good soil, 40 cm. apart in every direction. In the next spring, the weeds are removed with the hoe until the plants fully cover the ground.

For the propagation of wormwood *(Artemisia Absinthium*, L., *Compositæ)*, seeds are not used so often as pieces of old plants or suckers. Young plants, growing between the rows from seeds fallen down, may likewise be taken for the purpose. Wormwood is satisfied with inferior soil that need not be black, as the fields in Thuringia show. Hoeing once is enough.

A discussion of a communication from B. Pater[1]) on spearmint and peppermint may here be joined on. He continued his former experiments[2]). The trial field bordered on a brook and was thus kept sufficiently moist. It had a light humus soil. The purpose was to find out, how the content of oil and its quality would be influenced by various manures. Cabbage had been grown there before, preceeded by turnips and marsh mallow. The field had been manured well in 1912. On 23th April 1914, suckers of spearmint, taken from other plantations the day before, were set after some artificial manure having been spread and raked in. Only part of the Chili saltpetre had been strewn; the remainder was put on afterwards as surface manure. Every plot was 360 sq. m. large. Pater manured each plot with 6 kg. of kainite, 15 kg. of superphosphate, 6 kg. of ammonia sulphate and 6 kg. of Chili saltpetre. Of the latter, only 4.8 kg. were given when planting, the remaining 1.2 kg. on July 18th as surface manure. It was necessary to weed early in June. The first cutting took place on August 29th, the plant material was dried on a loft up to September 29th and then distilled. The action of the potash manure was remarkable, a proof that mints make good use of it. The oil of the twelve plots was not uniform at all, but differed in colour and aroma. The finest, least coloured oil was obtained from the plot N° 2, which had been manured with potash (kainite); besides, the yield surpassed that of any other plot.

In 1915, the spearmint field was further observed and used, when it yielded 12.86 kg. of oil from 1195 kg. of dried herb = 1.07 per cent. In 1916, *i. e.* in the third year, the spearmint was again weeded and cut, but thereafter the plants grew so little that the fresh shoots barely reached a span's length and it would not have paid to mow them.

Manuring experiment with spearmint.

Number of plot.	Manure.	Crop of fresh herb.	Crop of dry herb.	Classification of plot according to crop.	Yield of oil.	Classification of plot according to yield of oil.
1	unmanured	86 kg.	24 kg.	12	257 cc.	12
2	40 per cent. kainite	195 „	43 „	1	603 „	1
3	superphosphate	133 „	39 „	4	561 „	3
4	Chili saltpetre	125 „	38 „	7	573 „	2
5	ammonia sulphate	111 „	32 „	8	444 „	7
6	kainite + superphosphate	97 „	26 „	11	343 „	11
7	kainite + Chili saltpetre	131 „	35 „	5	403 „	9
8	kainite + ammonia sulphate	129 „	34 „	6	534 „	4
9	superphosphate + Chili saltpetre	102 „	30 „	9	453 „	6
10	superphosphate + ammonia sulphate	99 „	27 „	10	397 „	10
11	kainite + superphosphate + Chili saltpetre	134 „	32 „	3	413 „	8
12	kainite + superphosphate + ammonia sulphate	147 „	40 „	2	534 „	5

Paters communications regarding his manuring experiments with Mitcham peppermint have been previously discussed in the main[3]). We now only wish to add that the plantation, started in spring 1914, was renewed in spring 1916, after the plants

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[1]) *Bericht über das Arzneipflanzenversuchsfeld der landwirtschaftlichen Akademie in Kolozsvár* (Report on the trial field for medicinal plants of Kolozsvár Academy of Agriculture) N° II, Kolozsvár 1917. — [2]) *Ibidem*, N° I, Kolozsvár 1914; *Report* April **1915**, 65. — [3]) *Pharm. Post; Seifensieder-Ztg.* **43** (1916), 365; *Report* October **1916**, 44.

had become weaker and paler already. The field was strongly manured in March and ploughed. The mint soon sent up fresh shoots and seemed refreshed, renewed and strengthened. The new shoots were dark in colour, a good many of them dark reddish brown.

Pater likewise continued his experiments with Japanese peppermint[1]). It withstood the severe winters quite well, so far, and could be propagated by means of seeds as well as of suckers. The plants obtained that way had a different look, another oil content and the oil itself was different too, as stated already by Irk[2]).

In spring 1916, the Japanese mint was transplanted on another bed, which had previously been well manured. 2.5 kos. of ammonia sulphate had been used for the 302 qm. and, in addition, half the bed received 1.25 ko. of kainite in the middle of June. The plants developed specially well. They were cut twice in the course of the summer and distilled in a fresh state. The half of the bed that had been manured with potash yielded 73 kos. of fresh herb for the first cutting (middle of July), *i. e.* 3 kos. more than the other half, on which no potash had been used. The yield in oil was 0.15 per cent. for either. In the beginning of September, the mint began to flower and was attacked by rust. Middle of September, the second crop took place, when the bed without potash yielded 58 kos. of herb with 0.189 per cent. of oil and the bed manured with potash 59 kos. of herb with 0.169 per cent. of oil. It seemed that the oil content of the Japanese peppermint had not decreased since 1913.

Finally, Pater mentions the degeneration and variability of cultivated mints, which starts as soon as the soil is not sufficiently rich in nourishment or does not come up to the requirements of the mint in other respects. The degeneration is noticeable not only in the look of the plant but also in the smell and specially in the quantity and quality of the oil. Degeneration, therefore, is one of the most important questions of mint growing. The study of this peculiarity is all the more interesting, as, along with the degeneration, variation, atavism and other irregularities likewise occur, which sometimes give us a clue as to the origin and relationship of the cultivated mints. This brings the author upon the difficult ground of systematizing the *Mentha* species. He presumes that the Hungarian spearmint is most closely related to *Mentha viridis*, L., of which it is perhaps a variety, but originated on a vegetative way, as it is so stable and unchanging. The oil of Hungarian spearmint distinguishes itself by its extraordinary high contents of carvene[3]). Pater has cultivated Hungarian spearmint already since 1895; the plants have partly run to waste, but he has not noticed any case of atavism. However, only suckers were used for propagation. Whereas peppermint degenerated on a poor soil, spearmint remained constant. On an experimental field, there was a bed of spearmint in the neighbourhood of a peppermint bed. The peppermint showed signs of degeneration and took the spearmint aroma, so that the oil obtained became useless as a peppermint oil. The spearmint, on the contrary, did not suffer from the neighbourhood. It is to be recommended, in consequence, not to grow the two species side by side. Agnelli's peppermint degenerates strongly, when various types can be distinguished.

Pater obtained the best results with cultivating Mitcham peppermint, which reminds him in appearance of *Mentha aquatica*, L. and he thinks that it is descended from it. There are also variations of Mitcham peppermint. The colour of stalks and leaves changes as easily as with other cultivated sorts.

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[1]) Comp. *Report* April **1915**, 65. — [2]) *Pharm. Zentralh.* **55** (1914), 459; *Report* April **1915**, 34. — [3]) Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd ed., vol. III, p. 593.

According to Pater, Japanese peppermint has been obtained from *Mentha arvensis* by cultivation.

Furthermore, Pater states that, in 1916, he received suckers from peppermint grown in Russia (Wolhynia), which developed quite well on a trial field. To judge by its appearance, it would seem to be closely allied to the English peppermint and to be derived from *Mentha aquatica*. Its odour is strange, but agreeable.

J. Chevalier[1]), in a treatise on the cultivation and harvesting of medicinal plants, refers also to balm-mint and peppermint. As there is nothing new in it, we refrain from going into details.

In an article worth reading, H. Zörnig[2]) makes communications of general interest regarding the cultivation of medicinal plants. He points out that the use of medicinal drugs has not decreased, as is often supposed, but that on the contrary it has risen considerably, not so much in the chemists shops, as by the consumption of an important branch of German chemical industry, *i. e.* that of manufacturing medicines and essential oils. He mentions briefly what has been undertaken in the various countries to foster the cultivation of medicinal plants. Germany has done very little in this respect[3]), whereas Austria and Hungary may be taken as models[4]). The cultivation of medicinal plants is likewise on a high level in the United States of North America, where a real army of scientific people are at work in order to raise it, starting from different points of view. Zörnig advocates that this example should be followed.

Essential oils from British East Africa. — On page 23 of our *Report* of October **1915**, we mentioned a geranium oil, distilled from fresh herb in Limoru (Brit. East Africa). It seems that this district, about 7000 feet high, is very suitable for growing aromatic plants. The climate is characterized by two rain periods. The district has copious rainfalls, generally speaking, and heavy dews[5]). Experiments have there been carried on with a bastard of *Lavandula vera* and *L. Spica*, called spike lavender. The oil of this hybrid showed d 0.894 and α_D — 10° 30′; it contained 3 per cent. esters and 44.1 per cent. alcohols. In consequence, it corresponds about in its properties with *"Lavandin"* oil[6]).

An oil of rosemary distilled there showed d 0.908; α_D + 1°. It contained 4,2 per cent. esters and 15 per cent. alcohols.

A sample of geranium oil contained only 12.1 per cent. esters and its odour was not specially agreeable.

Samples of lemon thyme oil[7]) contained 18 per cent. citral and 6 per cent. 6 phenoles.

The French crops of jasmine and tuberose in 1917. — Owing to the hard winter before last and to the unfavourable weather in spring 1917, the jasmine crop, ended on September 20th in the South of France, has remained below the average[8]). The prices

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[1]) *Bull. Sciences pharmacol.* **24** (1917), 46. — [2]) *Jahresber. d. Verein. f. angew. Bot.* **14** (1916), 57. — [3]) Comp. *Report* October **1917**, 110. — [4]) Comp. *e. g. Report* April **1915**, 67. — [5]) *Perfum. Record* 8 (1917), 263. — [6]) In the South of France, a cross between lavender (*Lavandula vera*, DC.) and spike lavender (*L. Spica* DC.) is called *"lavandin"*. It is the hybrid called *L. Burnati* by Briquet. Comp. Gildemeister and Hoffmann,' *Die ätherischen Öle*, 2nd ed., vol. III, p. 450. — [7]) It is not quite clear which plant is meant. Numerous subspecies of *Thymus Serpillum* have been described, of which *Thymus citriodorus*, Schreber, smells of lemon and is known by the name of lemon thyme. (Comp. Engler-Prantl, *Natürliche Pflanzenfamilien*, part IV, section 3 a and 3 b, Leipzig 1897, p. 312. — Thomé, *Flora von Deutschland*, vol. IV, Gera 1905, p. 101.) — [8]) *Seifensieder-Ztg.* **44** (1917), 1021.

reached 3 Francs per ko. early in August. The flowering was hastened by hot and dry weather. As the factory owners had been unable to get the fats ordered during the winter, they were forced to reduce the manufacture of pomades and to use the remainder of the crop for preparing cnncentrated essences. As a consequence, there was rather more life in the factories, as many unskilled hands had to be taken on. Generally speaking, the pomades were of good quality.

Last year's tuberose crop was a failure due to a severe disease of the flower-stalks.

The *ginger imports* into Great Britain are indicated as follows in the *Time Trade Supplement*[1]):—

From British possessions:—		
East India	27 931 cwts.	= 62.5 per cent.
West Indies	5 398 „	= 12.1 „ „
Sierra Leone	7 295 „	= 16.3 „ „
various colonies	3 377 „	= 7.6 „ „
total:	44 001 cwts.	= 98.5 per cent.
from non-British countries:—		
Japan	535 cwts.	= 1.2 per cent.
other countries	113 „	= 0.3 „ „
	648 cwts.	= 1.5 per cent.
total:	44 649 cwts.	= 100 per cent.
re-exports	21 418 „	= 48.0 „ „

The exports from British India exceed 3000 tons yearly, on an average. The finest ginger is grown by negroes on Jamaica, who export about 1200 tons annually. The Sierra Leone product has gone down in price considerably, owing to lack of care and to smuggling. The centre of ginger production is Canton.

Imports of cinnamon[2]) into Great Britain, in 1915, exceeded three times those of the previous years, the chief countries of origin being:—

Ceylon	2 937 000 lbs.	= 85.4 per cent. of the total imports
Seychelles	328 000 „	= 9.5 „ „ „ „ „ „
other British regions	167 000 „	= 4.8 „ „ „ „ „ „
foreign countries	8 000 „	= 0.3 „ „ „ „ „ „
total:	3 440 000 lbs.	= 100 per cent. of the total imports
re-exports	1 872 000 „	= 54.4 „ „

In Ceylon, vast tracts formerly used for growing cinnamon have been planted with cocoa-nut palms and rubber trees, as these require less care. Prices of cinnamon have gone down, since the cheap Chinese cassia bark has been used in many cases as a substitute for real cinnamon. In any case, the best cinnamon comes from Ceylon, as the taste of the bark never remains equally good, if the tree is transplated into other countries. Cinnamon is grown on Java too. An inferior quality, Padang cinnamon, is Annam's chief article of export. Only quite recently one has begun to cultivate the cinnamon tree in nurseries, whereas before it only grew wild in the woods.

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[1]) *Bulletin* of 7. 5. 18.; *Nachr. f. Hand., Ind. u. Landw.* **1918**, N° 69, p. 3. — [2]) The figures apparently refer to the so-called Ceylon cinnamon.

Nine tenth of the cloves come from Zanzibar and Pemba, the remainder being obtained in the Dutch Indies, on the Moluccas and on Madagascar. Zanzibar exported in 1913: —

	In quintals of 45 kos.
to India	57 274 quintals
„ Germany	38 010 „
„ Great Britain	28 115 „
„ the United States	17 639 „
„ France	4 241 „
„ Austria-Hungary	3 063 „
„ Italy	2 606 „
„ Holland	1 204 „
„ other countries	6 890 „
total:	159 042 quintals

The exports from Zanzibar amount to 90 per cent. of the world's total production. What formerly was destined for Germany is now shipped to the U. S. of North America.

Regarding the *essential oil industry in Andalusia,* we here insert an extract from an article by L. G. Dreyfus[1]), which is of general interest.

This industry is said to have been founded in Malaga, about 20 years ago. The quantities of oil obtained were quite small in the beginning, but the author asserts that they increased considerably especially since the beginning of the war, as the competition of the cheap German oils was no longer to be feared.

We absolutely fail to see what cheap German oils Dreyfus means. It is again one of those cases, where German goods are held responsible for everything.

In Malaga, there are two modern steam distilling plants, under the management of experienced chemists. One is a German, the other a Belgian concern. A third similar plant is situated in Jaen. Besides, there are hundreds of small distilleries, spread over the provinces of Malaga, Jaen and Granada, where stills holding from 100 to 500 lbs. of material are worked over direct fire. The oil thus obtained is considerably inferior to that produced by steam distillation in the modern plants. Peasants often have a still lent from a business man, on the condition that they exclusively sell to him all the output, at a price fixed beforehand.

Although there are no plantations of aromatic plants, there is never any lack of material for distilling, as the wild flora supplies it. The season for sage is from May to July, that for thyme and rosemary from July to September and that for fennel, spike lavender and lavender from September to November. In winter, when the material for distilling is scarce, the large factories make use of the time by rectifying the oils. Exports to America have risen considerably, these last years. The relative figures are: —

1898	179 $	1905	5455 $	1912	72034 $
1899	565 „	1906	— „	1913	76966 „
1900	— „	1907	1231 „	1914	83773 „
1901	669 „	1908	3902 „	1915	137129 „
1902	502 „	1909	3646 „	1916	176164 „
1903	— „	1910	10445 „	1917	200329 „
1904	— „	1911	23940 „	9 first months	

[1]) *Commerce Reports; Amer. Journ. Pharm.* **90** (1918), 276.

America's total imports from all countries of the oils exported from Malaga were: —

	fiscal year ending 30th June 1915	1916
fennel oil	441 $	789 $
juniper oil	7637 „	1988 „
lavender and spike lavender oils	117039 „	271815 „
origanum oil	15111 „	24291 „
rosemary oil	44636 „	30504 „
thyme oil	88498 „	85913 „
total:	273362 $	415300 $

The rosemary oil is intended for debasing olive oil; oil of thyme, for the manufacture of thymol.

The cultivation of aromatic plants in Australia. — Recently, the Victorian Scent and Essential Oil Association was founded in Melbourne[1]), whose object it is to further the cultivation of flowers for producing scents and essential oils, to obtain through united efforts suitable seeds and plants, to manufacture articles of commerce, to conquer the best markets, to lay out at general expense a trial garden for growing aromatic plants and to erect works for distillation of essential oils, as well as for their production by other means. State subvention will be applied for.

That the *industry of essential oils and aromatics in British India* is still on a very low level, may be supposed to be well known[2]). That such is the case can be clearly seen from J. P. Srivastava's[3]) article on the subject.

The native manufacturers had given up before the war all production of *"attars"* from fresh flowers, as it was far simpler to make them by perfuming odourless fatty oils with imported German artificial flower oils. As the arrivals from Germany ceased, owing to the war, more attention was paid again to the old methods. The centres of the perfumery industry are Kanauj, Jaunpur and Ghazipur. The distillation is carried out in a most primitive manner. The still consists of a vessel connected by means of a bamboo stick with the refrigerator, placed in a tub filled with water. The refrigerating pipe is not twisted. The vessel is placed on a hearth and filled with flowers, on which water is poured till they are covered. Heating is done on an open fire, and as there is no sieve-bottom in the vessel, the flowers burn quite frequently, which does not improve the product. Owing to leakiness and insufficient cooling, there are always losses of volatile aromatics. It would be easy to improve the distilling apparatus, but most of the producers are extremely conservative and decline all innovations. The Indian perfumery industry produces specially *attars*, perfumed waters and oils.

According to Srivastava, one understands by *attars* products made of sandalwood oil and other, specially odoriferous oils. For this purpose, the ordoriferous essential oil is distilled into a receiver filled with sandalwood oil. The *"attars"* are mostly prepared from roses, *"keora"*[4]), *"henna"*[5]), *"khus"*, *"joohee"* &c.

The scented waters are the by-products of distillation; especially those of roses and *"keora"* are in good demand.

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[1]) *Perfum. Record* **9** (1918), 106. — [2]) Comp. *Report* October **1917**, 32. — [3]) *The Wealth of India* (Madras, March **1917**); *Perfum. Record* 8 (1917), 188. — [4]) According to Dymock, Warden and Hooper (*Pharmacographica indica*, vol. III, p. 535, London, Bombay, Calcutta 1893) *Pandanus odoratissimus*. — [5]) According to Dymock *Lawsonia alba*.

Perfumed oils are obtained by *"enfleurage"*. For this purpose, carefully cleaned and shelled sesame (*"til* seeds")[1]) are used and the oil pressed from them afterwards contains the odours of the flowers. The products thus obtained are far superior to the distilled ones.

Srivastava says that *"attars"* are prepared in British India in a most thriftless and unscientific way, as the apparatus available is quite unsatisfactory.

As sandalwood oil has become very dear, the author recommends palmarosa oil as a substitute, provided it was possible to remove its pronounced odour.

It seems to be difficult to get odourless alcohol in India, the home product being useless for perfumery.

The modern European methods of *"enfleurage"* have not been tried yet in India. It is impossible to use lard for the purpose, owing to the religons prejudice of the population. The above mentioned *"enfleurage"* with sesame seeds is unpractical, as the oil pressed from the seeds is coloured and contains impurities.

The exports of raw materials for perfumery from British India were as follows: —

	quantity in cwts.		value in £	
	1913/14	1914/15	1913 14	1914/15
ajama[2])	4507	2609	2953	2045
ajwain[2])	9784	7368	2983	2736
aniseed	1129	835	921	977
assalia[3])	505	170	418	133
coriander	95533	84058	39099	46327
cumin	19026	13554	29338	25698
nigella seed	1313	1411	1157	985
fennel	15256	4223	11348	3446
fœnum-græcum	12760	18300	7301	10161
dill	2090	1945	1489	1351
other seeds	147	99	192	43
total:	162050	134512	97209	93902.

The industry of essential oils and aromatics in France. — We beg to call our readers' attention to an article published under this title by K. Löffl[4]) and containing short notes on the manufacture as well as some statistical communications.

In some articles on the *industry of the "agrumen" by-products in North-America*, R. T. Will[5]) and F. A. Mc. Dermott[6]) describe the difficulties met with in the manufacture of preserved juice from oranges and lemons. Generally speaking, it seems to be difficult to prepare fruit juices that will keep, but it seems, as per a communication from H. Thoms[7]) that the question has been solved in a fairly simple way. Most of the fruit juices contain ferments, which after a comparatively short time lead to decomposition. In order to prevent fermentation, the fruit juices are sterilized and stored in sterile vessels, or they are boiled with sugar or preserved with salicylic acid. Through these methods, however, on the one side valuable aromatic substances are partly lost; on the other, the unstable ferments are destroyed, especially through sterilizing and boiling. Even boiling at a fairly low temperature *"in vacuo"* does not protect the ferments against decomposition, especially if the fruit juices are rich in acid, as is generally the case.

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[1]) According to Dymock *(loc. cit.) "til"* is the Hindoo or Bengal word for sesame. — [2]) According to Dymock *(loc. cit.)* the same as *"ajowan"*. — [3]) According to Dymock *Lepidium sativum*. — [4]) *Deutsche Parf. Ztg.* **3** (1917), 171. — [5]) *Journ. ind. and engin. Chemistry* **8** (1916), 78; *Report* October **1916**, 21. — [6]) *Journ. ind. and engin. Chemistry* **8** (1916), 136; *Report* October **1916**, 26. — [7]) *Berichte* **50** (1917), 1240.

By a process patented by him, Thoms prepares from the fruit juices an extract which contains unaltered all the aromatic substances and the ferments, in that he deprives the sour juices, obtained from the cut up, squeezed fruits, of their excess of acids through dialyzation in cooled rooms[1]). The aromatics and ferments do not pass through the membrane, but part of the acids. The juices are then boiled down to the consistency of extracts in vacuum apparatus free from metals at a temperature not exceeding 40°.

In that way, a most tasty pine-apple extract was obtained, with the ferments unaltered, as could be proved by digesting experiments with meat or albuminous substances, like ricine. The extract likewise possessed the full fruit aroma, as became specially noticable when diluting it with water or sugar solution. The contents of proteolytic ferments amounted to about 3.5 per cent.

Cultivation of aromatic plants in North America. — In a lecture delivered before the Manufacturing Perfumers' Association of New York, W. W. Stockberger[2]) reported on the work done by the Bureau of Plant Industry, Washington, DC., with regard to plants yielding essential oils.

Numerous aromatic plants are cultivated and distilled at Arlington Farm, Va., and for every species the conditions required, the adaptability to soil and climate, the yield of essential oil and the components of this oil are determined. If the prospects are favourable, the next important question will be to find a suitable district, where the economic conditions permit of founding an essential oil industry.

The success arrived at in the rose-garden are quite interesting. Only 41 out of 95 varieties cultivated have proved suitable for the manufacture of oil, the most promising being some varieties of *Rosa rugosa* and *Rosa centifolia*. For this summer, experiments with roses in the southern states are planned.

Lavender, caraway, anise, wormwood, various mints, rosemary and other plants yielding important essential oils are grown at Arlington Farm. Parallel experiments are being made in various parts of the United States. Some colleges and universities own gardens, in which they work hand in hand with the Bureau of Plant Industry. Stockberger mentions the investigation of oils from the various parts of the calamus plant carried out by G. A. Russell[3]) in Madison and the study of the oils of *Artemisia frigida*[4]), *Ramona stachyoides*[5]) and *Artemisia tridentata*[6]).

In Orlando, Florida, experiments have been made with various other plants, such as *Monarda punctata*[7]), lemongrass[8]), Ceylon cinnamon, cassia, *Pycnanthemum albescens*, *Illicium anisatum*, the clove tree, *Persea pubescens*[9]) and *Hedychium coronarium*. The production of camphor has likewise been studied with so much success as to permit of founding several considerable undertakings.

"The aromas of fermented liquids" is the title of an article published by K. Löffl[10]), in which our present knowledge of the subject, which is rather limited, is briefly described, without the addition of anything new.

In the introduction, be discusses the difficulties of classifying the aromas, mentions Zwaardemaker's work, but not Henning's[11]) latest investigations in this domain. He

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[1]) *G. P.* 285304 of June 20th 1914. — [2]) *Perfum. Record* **9** (1918), 100. — [3]) Comp. *Report* October **1916**, 8. — [4]) Comp. *Report* April **1912**, 26. — [5]) Comp. *Report* April **1912**, 107. — [6]) Comp. *Report* October **1917**, 4. — [7]) Comp. *Report* October **1916**, 78. — [8]) Comp. *Report* October **1917**, 27. — [9]) Comp. *Report* April **1912**, 105. — [10]) *Deutsche Parf.-Ztg.* **3** (1917), 180. — [11]) H. Henning, *Der Geruch* (the sense of smell), Leipzig **1916**; *Report* October **1917**, 123. — H. Henning, *Zeitschrift für Psychologie* **73** (1915), 161, **74** (1916), 305; **75** (1916), 177; *Report* October **1916**, 103.

points out that the wine aroma is not due to only one body, but to a whole range of odoriferous chemical compounds. The chief substance which gives the wine its aroma and distinguishes it from beer and other beverages is œnantic ether. At the end, he communicates some analyses of wine aromas, gathered from other publications.

R. Kissling[1]) reports on *aromatic and flavouring substances in the tobacco industry.* — Generally speaking, chemistry has attained extremely little or nothing, so far, in the domain of curing and improving tobacco. It is the same case with tobacco as with wine; the analytical chemist cannot determine the chemical constitution of the mixture of different substances to which the good tobaccos and wines owe their aroma. Nevertheless, aromatizing and curing act an important part in the tobacco industry.

Regarding tobacco for cigarettes, scarcely anything of importance can be said, as every cigarette factory keeps its recipes for flavouring the tobacco a perfect secret. An essential component of all such recipes, however, seems to be honey or a mixture of aromatic substances producing a similar odour. Extracts of sweet fruits are also used.

Tobacco for smoking is perfumed with drugs containing cumarin, such as tonca beans, sweet vernal grass *(Anthoxanthum odoratum)*, vanilla beans, &c., furthermore oils of lavender, cloves, cinnamon, sassafras, bergamot, citronella and similar aromatic substances.

Chewing-tobacco is likewise aromatized to a great extent with fruit extracts (from tamarinds, prunes, &c.), extracts from seeds and other materials containing essential oils. The recipes are kept quite secret by the manufacturers.

Such recipes are often intricate and out of date, so that it would be possible in many cases to improve them, but it must be taken into consideration that the customers are most conservative with regard to the aroma they are used to get.

Tables of essential oils. — In the *Deutsche Parfumerie-Zeitung*, A. Reclaire[2]) publishes tables of the essential oils described up to January 1917, with short notes as to the raw material, botanical origin, the specific gravity, the optical rotation in the 10 mm. tube, the constituents, etc.

L. Trabaud[3]) discusses all the *publications on essential oils and their components* that have appeared in 1914 and 1915. He not only takes into consideration the components of essential oils as such, but also derivatives of these bodies, which are of no direct interest to our industry, and other bodies contained in aromatic plants, that are not volatile.

A. Reclaire[4]) publishes a report on the progress made in 1916/17 in the *domain of the chemistry of the esssential oils and aromatics.* In addition to a discussion of the relative treatises published, a short resumen is given of the most important customs regulations. The same author[5]) is responsible for an article on the judgment of essential oils. As it does not contain any fresh points of view, we only just mention the article. Furthermore, he[6]) compiled a summary of all the decisions regarding customs tariffs and of all the official regulations published between July 1916 and August 1917, as far as the industry of aromatics and the soap industry are concerned, as well as an article on the influence of chemistry on the essential oil industry[7]).

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[1]) *Deutsche Parf.-Ztg.* **4** (1918), 28. — [2]) *Deutsche Parf.-Ztg.* **3** (1917), 138 and following pages. — [3]) *Rev. gén. de Chim.* **20** (1917), 39 and following pages. — [4]) *Zeitschr. f. angew. Chem.* **30** (1917), I. 217. — [5]) *Deutsche Parf.-Ztg.* **3** (1917), 185. — [6]) *Deutsche Parf.-Ztg.* **3** (1917), 230. — [7]) *Ibidem* **4** (1918), 1.

"Aromatic Chemicals and the Relations between Smell and Constitution" is the title of an article by H. J. Prins[1]), which does not lend itself to a short reproduction. We therefore beg to refer our readers to the original.

H. Schelenz[2]) reports on *perfumery in antiquity,* describing the most important cosmetics and scents then used. All those interested in the history of perfumery and cosmetics will find some useful information in the article.

Bibliographical Notes.

Last summer, the second volume of the third edition of J. von Wiesner's well-known work *"Die Rohstoffe des Pflanzenreichs"* (the raw materials derived from plants) was published by Wilhelm Engelmann in Leipzig. The first volume had been completed already in 1914. Wiesner, to whom science is greatly indebted, having died in October 1916, T. F. Hanausek and J. Moeller have been entrusted with the continuation and completion of his work.

A considerable part of the second volume is taken up by K. Wilhelm's chapter on the several kinds of wood and in which a good many plants are discussed that supply our industry with raw material. We would call attention to the following: On page 550 the so-called West-Indian sandalwood is spoken of as being of unknown origin, which is not correct, as it has been determined years ago beyond doubt that it comes from the *Rutacea Amyris balsamifera*[3]).

Messrs. R. M. Gattefossé and L. Lamothe's book (188 pages), entitled: *"Culture et Industrie des Plantes aromatiques et des Plantes médicinales de Montagne"* (Paris 1917) may be looked upon as an extended 4th edition of L. Lamothe's treatise *"Lavande et Aspic"*. Having fully discussed the 2nd edition at the time[4]), we may here be short. The chief part of the book is taken up by the cultivation of lavender (*Lavandula vera,* DC.) and its varieties and hybrids; then the cultivation of spike lavender, thyme, *Salvia sclarea,* rosemary, hyssop, camomile, lime-tree and angelica is dealt with.

A concise chapter refers to the lavender parasites and the little illustration given is meant to show the different stages of development of one such parasite. Experts[5]), however, have drawn the author's attention to the fact that the pictures do not represent one and the same insect at different stages, but the chrysalis of a small moth, two myriapodes *(Julus)* and a larva, probably of a beetle.

The third edition of E. J. Parry's well-known book "The Chemistry of Essential Oils and Artificial Perfumes"[6]) has appeared and is announced in J. C. Umney's[7]) "Perfumery and Essential Oil Record": In this connection, Umney also mentions Gildemeister and Hoffmann's work *"Die ätherischen Öle"* (The Volatile Oils), stating that it had not been translated into English as yet. This is a mistake, however, for the first two volumes have been published in English in 1913 and 1916, respectively, the former having even been discussed at the time in the "Perfumery and Essential Oil Record"[8]).

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[1]) *Perfum. Record* 8 (1917), 222. — [2]) *Deutsche Parf.-Ztg.* **4** (1918), 83. — [3]) E. M. Holmes, W. Kirkby and A. Petersen, *Pharm. Journ.* III. **16** (1886), 757, 821, 1065; **62** (1899), 53, 137, 205. — Comp. Gildemeister and Hoffmann, *Die ätherischen Öle,* 2nd ed., vol. III, p. 114. — [4]) Comp. *Report* November **1908**, 76. — [5]) *Parfum. moderne* **11** (1918), 5. — [6]) Comp. *Report* October **1909**, 108. — [7]) *Perfum. Record* **9** (1918), 81. — [8]) *Perfum. Record* **4** (1913), 308.

Analytical Notes.

The *estimation of the alcohol content of essential oils* by the acetylation method is effected, as is generally known, by means of the formula: —

$$\text{per cent. alcohol in original oil} = \frac{a \times m}{20 \times (s - a \times 0.021)},$$

in which

m = molecular weight of the alcohol calculated,
a = amount of c. c. seminormal caustic potash solution,
s = weight in grams of acetylated oil used.

In Gildemeister's text-book *The Volatile Oils* (1910), 2nd edition, vol. I, p. 576, it has been stated, when discussing the above formula, that a possible content of primarily esterified alcohols in the oil is herein not taken into account. Consequently, the values calculated are generally found to be too high. In such cases, when the ester content of the oil is low, the error is but insignificant and for practical purposes need not be taken into consideration. The difference, however, increases in proportion to the ester content and must then be eliminated. To this end, we suggested the following *modus procedendi*: — From the difference of the ester values of the original and the acetylated oil, the amount of *free* alcohols in the oil is calculated, then amount of *combined* alcohols, such as found by the ester value of the original oil, is added thereto, thus giving the amount of *total* alcohols in the oil.

The results obtained by this method are likewise not quite correct, since the ester value is calculated the first time from the original oil, for the second time from the acetylated oil. This discrepancy is taken into account by a new formula worked out recently by T. Tusting Cocking[1]), which therefore gives quite exact results. The formula runs as follows: —

$$\text{per cent. of alcohols in original oil} = \frac{m \times (\text{E.V. II} - \text{E.V. I})}{0.42 \times (1333 - \text{E.V. II})}$$

in which

m = molecular weight of alcohol calculated[2]),
E.V. I = ester value of the original oil,
E.V. II = ester value of the acetylated oil.

This formula is based on the following consideration.

One g. of oil gains x g. by acetylation, owing to addition of CH_3COOH and loss of H_2O. The increase is CH_3CO with the molecular weight 42 corresponding to 56 g. KOH, so that 1 g. CH_2CO equals 1.333 g. KOH, in other words, the ester value of CH_2CO is 1333.

Now, 1 g. original oil require . . . E.V. I mg. KOH
1 g. acetylated oil require . . E.V. II mg. KOH
1 g. C_2H_2O require . . . . . 1333 mg. KOH.

Hence, 1 g. original oil + x g. C_2H_2O require (E.V. I + 1333 x) mg. KOH. Furthermore, 1 g. original oil + x g. C_2H_2O correspond to (1 + x) g. acetylated oil, and since (1 + x) g. acetylated oil require (1 + x) × E.V. II mg. KOH, there results

$$\text{E.V. I} + 1333\,x = (1 + x) \times \text{E.V. II},$$

from which follows: —

$$x = \frac{\text{E.V. II} - \text{E.V. I}}{1333 - \text{E.V. II}}.$$

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[1]) *Perfum. Record* 9 (1918), 37. — [2]) In the original paper, the atomic weights are calculated on the basis of O = 16. In correspondance to the formulæ employed elsewhere in Gildemeister's text-book, we substitute here the round atomic weights — the slight differences arising thus are of no importance for the result. For the same reason, we have chosen different abbreviations as has the original work.

Now, the weight of the C_2H_2O added is molecularly proportional to the free alcohol present in the original oil,

$$m : 42 = \text{alcohol in 1 g. oil} : x,$$

so that the weight of the free alcohol in 1 g. oil

$$= \frac{m \times x}{42} = \frac{m \times (\text{E.V. II} - \text{E.V. I})}{42 \times (1333 - \text{E.V. II})}$$

hence the percentage of free alcohol

$$= \frac{m \times (\text{E.V. II} - \text{E.V. I})}{0.42 \times (1333 - \text{E.V. II})}.$$

As dealt with above, with low ester content in the oils the differences in the values are only slight, so that from a purely practical point of view we suggest to continue stating the oil content of total alcohols without taking into consideration the esters present in the original oil, *i. e.*, to state the values found straight from the E.V. of the acetylated oil. Only with oils rich in esters, such as geranium oil, considerable discrepancies become manifest, and in such cases, we admit, it is recommendable to state, in addition to the apparent content of alcohols as calculated from the ester value after acetylation, the correct alcohol content, such as calculated by Tusting Cocking's method.

The only method for the determination of the *volatile oil content of citrus* fruits is, as C. P. Wilson and C. O. Young[1]) have found, distillation of the ground fruits with steam. Several attempts were made to extract the ground peel by means of some organic solvent, such as alcohol, ether, benzene, gasoline, chloroform, or carbon tetrachloride. It was found, however, that invariably a large amount of water was dissolved by the solvent, even when benzene, carbon tetrachloride, or similar solvents were used. No practical method was found to drive off this water without loss of oil. The authors then tried to mix the ground peel with anhydrous copper sulphate or sodium sulphate and to extract the mixture as before; but ton large amounts of dehydrating material were required, which caused packing or caking and prevented complete extraction.

The most satisfactory method was as follows:— The whole fruit is passed three times through a fine cutting food grinder mixed thoroughly; immediately after grinding, 200 g. of the sample is weighed into a $1^1/_2$ liter flask and mixed with 700 cc. of water. The oil is then rapidly distilled off by steam, tho flask being gently heated; the distillate is collected in a special oil flask resembling a Babcock milk test bottle, the body of which had a capacity of 200 cc., the neck 2 ccm., the latter being graduated in $^1/_{10}$ cc. As soon as the distillation of the oil is complete, the oil is brought into the graduated neck of the bottle by addition of water and whirled in a centrifuge until all of the oil has collected in a clear layer. The volume of the oil is read off and the weight calculated by the formula Weight = Volume $\times$ 0.849 $\times$ 0.996, where 0.849 is the mean specific gravity for California lemon oils, and 0.996 the factor correcting for determinations made at 25°/25° C. in air. In exact work, the specific gravity of the oil should be predetermined for the particular kind of fruit used.

When the ground peel alone is distilled, and the percentage calculated back to the entire fruit, the results obtained are usually too low owing to the loss of oil during the peeling.

Ten samples of the Californian Eureka lemon gave distilled oils with specific gravities, at 25°/25° C., from 0.8462 to 0.8504, average 0.8487; 12 samples of the Lisbon

[1]) *Journ. ind. eng. Chemistry* **9** (1917), 959.

lemon showed 0.8434 to 0.8511, average 0.8484; three samples of the Villa Franca lemon gave 0.8485 to 0.8508, average 0.8494. The general average was, as stated above, 0.8487.

Concerning the examination of so-called Swedish oil of turpentine, *vide* p. 26.

Methods for quantitative estimation of chlorine in benzaldehyde are dealt with on p. 61 of this *Report*.

Estimation of camphor in solution with fatty oils. — The process adopted by the German Pharmacopœia for the estimation of camphor in *Oleum camphoratum* (the oil is heated on a water bath for one hour and must lose about one-tenth of its weight) is incorrect; in addition, the time given is too short. For this reason, O. von Friedrichs[1]) suggests measuring the optical rotation, a method which is applicable whenever natural camphor of high rotatory power is used. He investigated camphor oils composed of olive, colza, or sesame oils with increasing amounts of camphor varying from 2 to 25 per cent., and found *e. g.* for

1. camphor in olive oil . . 10 per cent.: + 10.22°; 20 per cent.: + 20.42°;
2. camphor in colza oil . . 10 per cent.: + 9.77°; 20 per cent.: + 18.86°;
3. camphor in sesame oil . 10 per cent.: + 11.56°; 20 per cent.: + 21.55°.

With olive oil, the percentage may be calculated according to the equation: $p = 1.958 \times \frac{\alpha}{l}$, with colza oil: $p = 1.963 \times \frac{\alpha}{l} + 0.41$, with sesame oil: $p = 2\frac{\alpha}{l} - 1.56$, where α = angle of rotation, l = length of rotation tube in decimeters. The reading is somewhat influenced by the temperature; a solution of 20 per cent. camphor, for instance, showing at 14° + 20.285°, rotated at 20°: 20.395, and at 24°: 20.480.

For the purpose of *identifying phenols*, E. E. Reid[2]) makes use of *p*-nitrobenzyl bromide, which reacts cleanly and quantitatively with alkali phenolates. The ethers resulting crystallize easily from dilute alcohol, melt sharply, and are suitable for identification purposes. The following ethers were prepared by the author: — the *p*-nitrobenzyl ethers of phenol (m. p. 91°), *o*-cresol (m. p. 89.7°), *m*-cresol (m. p. 51°), *p*-cresol (m.p. 88°), thymol (m.p. 85 5°), eugenol (m.p. 53.6°), and vanillin (m.p. 124.5°).

As to the identification of phenol (carbolic acid) and of methyl *p*-hydroxybenzoate in oil of wintergreen, see p. 64.

Concerning the estimation of thymol, *vide* p. 70 of this *Report*.

Estimation of butyric acid and of other fatty acids. — Many years ago, Duclaux[3]) has worked out a method for the estimation of volatile acids in mixture with alcohols, as frequently produced by action of bacteria. The first distils the alcohol from the neutralized liquid, then adds a solution of tartaric acid and distils the acids off by fractionation in this manner that from 110 cc. of the liquid the distillate is collected in fractions of 10 cc. each, each of which is dissolved in standardized alkali solution; thus 10 fractions of 10 cc. are obtained. The saturation of the alkali (Duclaux prefers lime water) manifests itself by the change in colour of the indicator added, *e. g.*, litmus. The first fractions contain the more volatile acids, the later fractions the less volatile

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[1]) *Svensk Farm. Tidskr.* **1918**, No. 12, p. 197; *Apoth. Ztg.* **33** (1918), 227. — *Schweiz. Apoth. Ztg.* **56** (1918), 450. — [2]) *Journ. Amer. chem. Soc.* **39** (1917), 304; *Zeitschr. f. angew. Chem.* **30** (1917), II. 379. — [3]) *Ann. Inst. Pasteur* **9** (1895), 265; *Chem. Zentralbl.* **1895**, I. 1086.

ones. By means of a table constructed by Duclaux or of a graph indicating the acidity degree of each of the fractions, the acid content of the latter may be calculated and conclusions drawn as to the nature of the separate acids (formic, acetic, propionic, butyric, valeric acids).

F. W. Upson, H. M. Plum and J. E. Schott[1]) have tested the constants worked out by Duclaux for formic, acetic, and propionic acids and found that exact values can not be arrived at by his method. Whenever two acids are present in the mixture, the results calculated are rather unreliable, and if one of the acids is present in the mixture only in a minor degree, each of the distilling fractions contained some of this acid. On the other hand, A. R. Lamb[2]) has found Duclaux' method to give satisfactory results in case the working conditions are strictly adhered to, the heating is effected by electricity and in case not more than two or three acids are tried to be determined in one fraction. In determining the constants of the acids, careful purification of the latter is essential.

According to H. Droop Richmond[3]), Duclaux' method is useful for determining butyric acid in acetic anhydride, and by combining Duclaux' process with the usual titrimetric methods a sample of acetic anhydride may be assayed as to its content of anhydride, acetic and butyric acids.

Furthermore, it might here be mentioned that J. K. Phelps and H. E. Palmer[4]) have designed a method for separating and estimating butyric acid. From a mixture with formic and acetic acids the former may be separated by means of its quinine salt, soluble in carbon tetrachloride, the quinine salts of formic and acetic acids being insoluble in that solvent. By weighing the quinine butyrate (m. p. 77.5°), the amount of butyric acid may be calculated. The quinine salt of propionic acid shows nearly the same solubility in carbon tetrachloride as the butyrate.

Nothing is stated in the abstract available whether it is a matter of normal or of *iso*butyric acid.

Another method for identifying and estimating butyric acid has been described by G. Denigès[5]). It is based on the formation of acetoacetic acid by treatment of butyric acid with hydrogen peroxide in presence of ferrous salts acting as catalysts, as stated by Dakin, and on the identification of the acetoacetic acid by means of sodium nitroprussiate. The mixture containing butyric acid is heated for 5 minutes to 70° with a certain amount of hydrogen peroxide and a solution of ferrous ammonium sulphate acidulated with sulphuric acid; then a few drops of caustic soda lye are added, the solution cooled down and filtered and a certain proportion of the filtrate is mixed with some drops of caustic soda solution, a few drops of a 5 per cent. sodium nitroprussiate solution and a slight excess of acetic acid. There results a red coloration, the intensity of which is in proportion to the butyric acid present; the amount of the latter may be estimated by comparison with solutions of known strength.

R. D. Crowell[6]) has worked out a process for estimating butyric acid in presence of acetic and propionic acids basing mainly on the fact that the principal amount of the butyric acid, besides some of the propionic acid, may be shaken out with petroleum (b. p. 150 to 300°) from the mixture of acids after saturation with calcium chloride and some potassium chloride. It would be beyond the scope of the *Report* to deal further with this rather complicated method.

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[1]) *Journ. Amer. chem. Soc.* **39** (1917), 731; *Journ. chem. Soc.* **112** (1917), II. 277. — [2]) *Journ. Amer. chem. Soc.* **39** (1917), 746; *Journ. chem. Soc.* **112** (1917), II. 277. — [3]) *Analyst* **42** (1917), 133; *Journ. chem. Soc.* **112** (1917), II. 277. — [4]) *J. Biol. Chem.* **29** (1917), 199; *Journ. chem. Soc.* **112** (1917), II. 278. — [5]) *Ann. Chim. analyt. appl.* **23** (1918). 27; *Chem. Zentralbl.* **1918**, I. 1073. — [6]) *Journ. Amer. chem. Soc.* **40** (1918), 453.

Identification of hydrocyanic acid for toxicological purposes. — In 1915, P. Lavialle and L. Varenne[1]) published a short notice on the above subject by means of the ferri-sulphocyanate reaction, where the acid or the solution of the cyanide is evaporated after addition of ammonium sulphide. The presence of formic or acetic acid is of no importance. The reaction is so exact that even an amount of sulphocyanic acid corresponding to 0.000054 g. hydrocyanic acid may be identified thereby, the method thus being twenty times more sensitive than the Prussian blue reaction. In order to avoid losses, the authors[2]) have designed a modification by using calcium polysulphides in lieu of ammonium sulphide. It would lead us too far to describe all the particulars of the method, and we refer our readers to the original paper; anyhow, since hydrocyanic acid is found frequently in the vegetable kingdom, and occurs sometimes when distilling certain plant stuffs, we wish to take short notice of this work.

For the *identification of hydrocyanic acid*, a variety of methods is known. Two authors, G. W. Anderson[3]) and I. W. Kolthoff[4]) deal critically with these methods, starting frown own investigations. According to these authors, the sensitiveness of the different reactions is as follows:—

Sensitiveness measured in mgrms. CN per litre:—

	Anderson	Kolthoff
Prussian blue reaction . . .	2.4 to 3.9 mgrm.	2 mgrm. per litre
Thiocyanate reaction	0.39 mgrm.	0.1 „ „ „
Pieric acid reaction	39 „	1 „ „ „
Guajac resin reaction	0.039 „	± 0.004 „ „ „
Phenolphthalein reaction . .	—	0.1 to 0.05 „ „ „
Silver cyanide reaction . . .	—	1 to 0.03 „ „ „
Iodine-and-starch reaction . .	0.39 „	0.1 „ „ „

According to these statements, Schönbein and Pagenstecher's guajac resin reaction would appear to be the most sensitive, hence preferable, reaction, but incorrectly, since (as Kolthoff remarks) this reaction is, generally spoken, not typical. Several bodies with oxidizing qualities (*e. g.*, the halogens, ozone) and indifferent substances (ammonia, cigar smoke) give the reaction likewise. A negative reaction, according to Dragendorff as well as to Anderson, proves the absence of hydrocyanic acid; Kolthoff disapproves of this, as some substances with reducing power inhibit the reaction.

Hydrogen sulphide interferes with the phenolphthalein reaction and must be removed with a cadmium solution. Inasmuch as chlorine, bromine, and hydrogen peroxide do not show a red coloration, this reaction is more typical than the preceding one; anyhow, larger amounts of the substances mentioned may inhibit the reaction.

The silver cyanide reaction is not specific for hydrocyanic acid. If chlorine be present, the distillation may be repeated from a solution of borax.

The iodine-and-starch reaction is neither typical, as several bodies of reducing qualities are likewise capable of binding iodine. If, however, the solution is acidulated afterwards, a blue coloration may be taken granted as proof for the presence of hydrocyanic acid, the reaction being typical with the aqueous distillate.

The picric acid reaction, generally spoken, is not typical, since it is given by many substances with reducing power, such as sulphurous acid, hydrogen sulphide, acetone,

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[1]) *Journ. d. Pharm. et Chim.* VII. **12** (1915), 74. — [2]) *Ibidem* VII. **17** (1917), 97. — [3]) *Journ. Soc. chem. Industry* **36** (1917), 195. — [4]) *Pharm. Weekblad* **54** (1917), 1157; *Apotheker Ztg.* **32** (1917), 529.

aldehydes, etc. Hydrogen sulphide may be eliminated by means of a cadmium solution. However, many organic bodies are apt to show the reaction, so that a negative result is of more importance than a positive one.

The Prussian blue reaction is specific to hydrogen cyanide and must be carried out with each test.

The same applies to the sulphocyanate reaction; some parts of the body, however, contain sulphocyanates, so that hydrogen sulphocyanate may pass over into the distillate, which then must be tested for by ferric chloride. In case of a positive reaction the hydrogen cyanide must be redistilled from a borax solution.

As to the determination of the cinnamic acid content in storax, *vide* p. 66.

Physical Notes.

C. Harries and R. Haarmann[1]) describe a laboratory-scale apparatus for steam distilling *in vacuo*. They make use of steam of 3 to 4 atmospheres pressure and conduct it through a round-bottomed flask acting as receiver for the condensed water and then through a reducing valve to a superheater. Between the latter and the flask serving as receptacle for the substance, a thermometer is inserted for measuring the temperature of the superheated steam. The flask is equipped with a head filled with glass tubing in order to avoid foaming and carrying over of drops during distillation and mounted with a thermometer for reading off the temperature of the liquid distilling. The long condenser is followed by a worm condenser leading to the receiver.

An efficient apparatus for fractional distillation under diminished pressure has been devised by W. A. Noyes and G. S. Skinner[2]). It consists of a 50 cc. bulb with rather narrow neck, probably for inserting a capillary tube or adding splinters of porous tile. On the one side of the flask there is arranged a separatory funnel of 50 cc. with glass stopcock, on the other side a high fractionating column with a great number of indentations distributed regularly on the stem. The funnel with stopcock offers the advantage of refilling the bulb without losing the vacuum.

E. Hildt[3]) has constructed a new apparatus for fractionating petroleum and other volatile liquids. It comprises six fractionating flasks connected with each other which may be heated separately and bear a contrivance enabling automatical syphoning of the fractions. We refer to the description of the design in the original paper, where also an illustration of the rather complicated apparatus is given.

On page 114 of our last *Report* we dealt with a paper of H. Zwaardemaker[4]) on the phenomena of electric charging when odoriferous bodies are sprayed. Since that time, a paper on this subject has appeared from the pen of E. L. Backman[5]) from which it appears that Zwaardemaker's "spray electricity" is to be of a different nature from the ordinary "cascade electricity". The action of salts on electricity produced by spraying aqueous solutions of volatile bodies is opposite to their influence on "cascade electricity". Probably, volatilisation plays an important part in the origin

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[1]) *Berl. Berichte* **51** (1918), 788. — [2]) *Journ. Amer. chem. Soc.* **39** (1917), 2718. — [3]) Compt. read. **165** (1917), 790. — [4]) *Koninkl. Akad. van Wetenschappen te Amsterdam* **24** (1916), 1630; **25** (1916), 3, 512. — [5]) *Pflüger's Arch. d. Physiol.* **168** (1917), 351; *Chem. Zentralbl.* **1917**, II. 753.

of "spray electricity". A raise in temperature causes likewise an increase in "spray electricity". No direct relation between this phenomenon and the dielectrical constants of the different bodies could be traced, neither any such relation between surface tension and the quantity of "spray electricity".

A short time ago H. Rupe[1]) established the term of the "relatively abnormal dispersion of optical rotation" and made it clear by means of examples. He continued his investigations in common with L. Silberstrom[2]) and examined whether the abnormal discrepancies in the rotatory dispersion were based upon a selective absorption in the neighbourhood of the visible spectrum, in the same sense as Tschugaeff explains the phenomenon of Cotton[3]).

Their investigation dealt in the main with the four bodies mentioned in the earlier paper, *i. e., 2,6*-dimethylundecatriene-*2,8,10* (prepared from citronellal and magnesium-allylbromide), *2,6*-dimethyl-*8*-phenyloctadiene-*2,7* (from citronellal and magnesiumphenylbromide), menthyl *β*-phenylcinnamate, and diphenylmethylenecamphor. For sake of comparison, several other substances were also taken into consideration, which belong either to the same chemical series or were at least closely allied to them, but otherwise showed normal rotatory dispersion. Amongst these were: several menthyl esters, then the hydrocarbons with normal optical rotation prepared from citronellal and Grignard's salts which had been investigated by Rupe and Jäger[4]), and several esters of myrtenol, which are all characterized by a decided normal and similar rotatory dispersion, as had been demonstrated by the proceding paper. Furthermore, diphenylcamphomethane and some derivatives of methylenecamphor were examined.

None of the substances investigated showed a selective power of absorption; in all cases, the absorption curve took a more or less continuous course.

Amongst all substances hitherto examined, diphenylmethylenecamphor, a body of light-yellow colour, showed the highest degree of relatively abnormal rotatory dispersion.

Diphenylmethylenecamphor may be prepared following the directions of Haller and Bauer[5]); an easier method is the following: Sodium is added to a solution of camphor in dry toluene and heated until the metal is fused. Very soon, a vivid reaction takes place; the mixture is allowed to cool down in a current of hydrogen, then the toluene is decanted off and a solution of benzophenone in toluene is added, the whole shaken vigorously and heated to 120 to 130°. Unattacked camphor, borneol, and toluene are then removed by steam distillation and the residue recrystallized from alcohol; m.p. 113.5°, given by Haller and Bauer as melting point for diphenylmethylenecamphor. Diphenylcamphormethane melts, according to the same authors, at 106 to 107°; separately prepared samples showed different optical rotation.

Rupe and Silberstrom found for the two bodies prepared according to the two methods described by Haller and Bauer the identical melting point 135.5 to 136.5° and nearly the same dextrorotation. For the first, it could not be stated with certainty which is the reason for the great difference in the behaviour of the bodies prepared by Rupe and Silberstrom and by Haller and Bauer.

Menthol crystallizing in different forms. — Recent physico-chemical research has shown that chemical compounds crystallize in different forms much more frequently as

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[1]) *Liebig's Annalen* **409** (1915), 327; *Report* October **1915**, 63. — [2]) *Liebig's Annalen* **414** (1917), 99. — [3]) Comp. *Berichte* **44** (1911), 2023. — [4]) *Liebig's Annalen* **402** (1914), 149; *Report* April **1914**, 136. — [5]) *Compt. rend.* **142** (1906), 975.

hitherto was assumed. Especially, the investigation of organic bodies by means of the crystallo-microscope[1]) has proven that numerous bodies may be obtained in two or more different modifications when the experimental conditions are altered. Principally, the temperature is decisive for the change of one form into another one. This takes place also with menthol which, according to F. E. Wright[2]), crystallizes in at least four different forms discernible as α-, β-, γ- and δ-form. Of these, only one, the α-form of ordinary menthol, is stable in the temperature range between 0° and its melting point 42.5°. The other three forms are monotropic and show lower melting points: β-form, m.p. 35.5°; γ-form, m.p. 33.5°; δ-form, m.p. 31.5°. The unstable forms, on standing, pass over into the stable modification, the δ-form, *viâ* the β-form.

It was difficult to measure the angles of ordinary (α-form) menthol crystals; anyhow, it could be stated with certainty that the crystals belong to the hexagonal system, as had been demonstrated years ago by Des Cloiseaux[3]). Melted α-menthol, for which Wright found $n_{D25°}$ about 1.458, was lævorotatory, the crystals, however, showed a dextrorotation of the five-fold strength.

All the forms of menthol show the tendency to form radial spherulites when crystallizing.

With use of the petrographic microscope, the transformation of the separate modifications into the stable α-form could be observed easily, it was even possible to measure the rapidity of the transformation of the γ-form into the α-isomeride.

The occurrence of the separate modifications is principally dependent on the temperature down to which the melted menthol cooled. Between 42 and 38° principally α-menthol crystallizes out, between 30 and 18° the γ-form, and between 18 and 5° the β-form, and between 5 and 12° the δ-form.

Some years ago, C. Tubandt demonstrated that the *inversion of menthone* is a species of reversible reactions of the first order most admirably fit for kineto-chemical investigation. Reciprocal reactions may be measured in the same temperature range with equal exactness and readiness, so that in this case the theory of a monomolecular reciprocal reaction could be confirmed with the necessary degree of certainty by experimenting from both sides of the equation. Recently, W. A. Gruse and S. F. Acree[4]) have been working on the inversion of menthone and published their results under the title, "The reactions of both the ions and the molecules of acids, bases, and salts; the inversion of menthone by sodium, potassium, and lithium ethylates". They studied the inversion of *l*-menthone by the aforesaid ethylates in solutions of absolute alcohol at 25°, working in very low concentrations in order to avoid abnormal salt or solvent effects. When discussing Tubandt's work, Acree[5]) had expected that, in case the ethylate ion be the active principle for the inversion, the constant for this reaction would have to be the same one, independant on which of the three ethylates the calculation is based.

The measurements were performed with dilutions of 1:32 up to 1:512 at 25°. Conform with Acree's expectation, the identical activation constant of the ethylate ion

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[1]) For studying the formation and transformation of crystals, especially the liquid crystals, use is made of Lehmann's crystallization microscope, which consists in the main of an ordinary microscope, but with a contrivance to heat the test-object and, on the other hand, a contrivance to blow cold air on the same, in order to keep the temperature somewhat constant. Equally, the test-object may be cooled by means of a current of water. — [2]) *Journ. Amer. chem. Soc.* **39** (1917), 1515. — [3]) *Compt. rend.* **70** (1870), 1211. — [4]) *Journ. Amer. chem. Soc.* **39** (1917), 376. — [5]) *Amer. chem. Journ.* **48** (1912), 359; *Chem. Zentralbl.* **1912**, II. 2040.

was found, with sodium, potassium, or lithium ethylate, to be $K_i = 0.501$, 0.501, and 0.496 respectively.

The constants for the activity of the non-ionized molecules of sodium and of potassium ethylates were practically identical, *i. e.*, $K_m = 0.693$ and 0.701. With lithium ethylate, K_m amounted to 0.478, a value nearly equal to that of the ethylate ion of lithium ethylate, 0.496.

Colloidal solution of camphor in common salt solution. — When *Oleum camphoratum* is shaken with water or with 0.75 per cent. salt solution, camphor is not dissolved in the water, but the camphor passes over in the colloidal state into the aqueous liquid, as H. Bordier and C. Roy have shown recently[1]). A mixture of *Ol. camph.* with water previously shaken with olive oil shows on examination in the ultramicroscope no mobile particles; when, however, *Ol. camph.* is shaken with water, numerous ultramicroscopical particles consisting of camphor are observable in the water.

In order to ascertain the amount of camphor passing as colloid into the aqueous solution on shaking *Ol. camph.* with salt solution, 500 cc. salt solution of 0.75 per cent. strength ("sérum artificiel") was left for 48 hours at 37° in contact occasional skaking, with 50 cc. *Ol. camph.* ($d_{15°}$ 0.921) containing for each 9 g. of olive oil 1 g. camphor. After 24 hours clearing, 336 cc. of the aqueous layer were extracted with 25 cc. benzene. The latter showed in a 20-cm. tube a dextrorotation of 43 minutes, corresponding to an amount of 0.335 g. camphor in 500 cc. salt solution.

It may be expected that after hypodermic injections of *Ol. camph.* camphor passes over into the blood in the colloidal state, and the authors are of opinion that the therapeutical effect of the remedy is mostly due to this physical phenomenon.

The physical properties of some absolutely pure esters of aliphatic acids have been determined by J. H. Matthews and K. E. Faville[2]). The esters, obtained from Kahlbaum, were purified according to Young and Thomas' directions[3]), consisting in the main in removing the free acids by shaking with aqueous potassium carbonate and extracting the remaining water and alcohol by treatment with dehydrated potassium carbonate and phosphorus pentoxide, after which the ester is fractionated carefully. The constants determined by Matthews and Faville are as follows: —

	B. p. at 760 mm.	$d_{4°}^{20°}$	n_D
*Iso*amyl formiate . . .	123.46 to 123.56°	0.8773	1.39772
*Iso*butyl formiate . . .	98.15 „ 98.25°	0.8832	1.38568
Propyl acetate	101.57 „ 101.77°	0.8869	1.38422
Ethyl propionate . . .	99.12 „ 99.22°	0.8904	1.38414
Propyl propionate . . .	121.0 „ 121.25°	0.8809	1.39325
Ethyl butyrate	120.0 „ 120.5°	0.8784	1.40002
*Iso*butyl valerianate . .	167.0 „ 168.5°	0.8544	1.40569

Hydrates of formic acid. — W. Oechsner de Coninck[4]) undertook the task of studying the behaviour of mixtures of water and formic acid on distillation. From a mixture of 25 cc. formic acid and 5 cc. water the principal portion distilled over at 107 to 108°, which seemed to consist of a hydrate of the composition $4HCOOH + 3H_2O$. Theoretically, the hydrate should contain 77.31 per cent. formic acid and 22.69 per cent. water;

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[1]) *Compt. rend.* **164** (1917), 648. — [2]) *Journ. physical. Chem.* **22** (1918), 1; *Journ. chem. Soc.* **114** (1918), I. 153. — [3]) *Ibidem* **63** (1893), 1191. — [4]) *Rev. gén. de Chim.* **19** (1916), 68.

found, 77.38 per cent. acid, 22.60 per cent. water. The same hydrate has been obtained formerly by Roscoe in a different manner; he states the boiling point to be 107.1 to 107.5°. On repeated distillation the hydrate splits off formic acid and seems to pass over into the hydrate $3HCOOH + 3H_2O$.

Investigations as to the *physico-chemical behaviour of camphoric* and iso*camphoric acids* have been carried out by Zehrfeld and Thoms; *vide* p. 140 of this *Report*.

Botanical Notes.

Experts do not agree as to the botanical origin of *Lignum nephriticum*. H. S. Möller[1]), at the time, arrived at the conviction that the *Lignum nephriticum mexicanum* came from the *Leguminosæ Pterocarpus Amphymenium*, DC., and *Pt. orbiculatus*, DC., the *Lignum nephriticum Philippinense*, however, from other kinds of *Pterocarpus*. According to Small and Stapf[2]), this is not the case and the *Leguminosæ Eysenhardtia amorphoides*, H. B. et K. is supposed to be the plant from which the drug is derived. W. E. Stafford[3]) thinks that both views are correct. He proves that there are two kinds of *Lignum nephriticum*, one of which, the Mexican, really comes from *Eysenhardtia amorphoides*, H. B. K. (= *E. polystacha*, Sargent). The other, sent from the Philippine Islands to Europe via Mexico, is supplied by *Pterocarpus indicus*, Willd. Both kinds of wood, above all the heartwood, impart to water the quality of fluorescing with a blue colour, whereas it looks yellow when the light passes through. The extract may be of little value as a diurectic, but the colouring matter deserves all phytochemical attention with regard to the presence of similar substances in many other tropical leguminous plants, especially kinds of *Pterocarpus*, such as *Pt. marsupium*, supplying kino, and *Pt. santalinus*, from which the red sandalwood is derived.

Occasionally only, one finds in books and other publications remarks on the germination of aromatic and medicinal plants, but not very much is known on the subject, although a knowledge thereof must be of the greatest interest to everybody connected with the cultivation of such plants. In a treatise entitled *"Über die Keimungsverhältnisse der Samen der gebräuchlichsten Arzneipflanzen"* (On the conditions of germination of the seeds of the current medicinal plants), G. Gentner[4]) discusses all that has been published so far about this important subject. There are a good many indications concerning our special domain.

As many medicinal plants are descended from wild species, which have been cultivated for a short time only, their seeds want special conditions for germinating and do not fit at all into the scheme, which we are used to form on account of the experiences made with the ordinary cultivated plants. There are seeds of wild plants that lose the faculty to germinate already 10 days after having ripened, *e. g.* most of our willows, and among our medicinal plants there are also some, such as angelica, the seeds of which retain their germinative faculty for a comparatively short time. Other seeds, on the contrary lie in the soil for months, even years, until they germinate.

Furthermore, it has been found that some seeds germinate only in a normal way in the dark, whereas others would then lie for months without showing any signs of

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[1]) *Berichte d. deutsch. pharm. Ges.* (Reports of the German Pharmaceutical Society) **23** (1913), 88; *Report* October **1913**, 69. — [2]) *Pharmaceutical Journ.* **92** (1914), 4; *Report* April **1914**, 68. — [3]) *Ann. Rep. of the Smithsonian Inst.; Pharm. Weekblad* **54** (1917), 1187. As per *Apotheker-Ztg.* **32** (1917), 519. — [4]) *Heil- und Gewürzpflanzen* **1** (1917), 16, 39, 77.

life and can develop their germs only in the light. A low temperature also has a great influence on the germination of some seeds. There are such as will germinate only after having been exposed for some time to the wintery cold, others must even get frost-bitten in several winters in order to germinate fully. Sometimes, it is the abrupt change of warm and cold that starts the germination.

Many experienced growers indicate that the seeds of a good number of plants germinate quickly and surely only if sown immediately after the harvest. An important criterion for the value of seeds is their being healthy. It occurs rather frequently that the seeds carry bacteria which attack the young plants or destroy the germs. They can be killed by treating the seeds with mercurials.

A review of the aromatic plants discussed by Gentner now follows.

The male fern *(Aspidium filix mas,* L., *Polypodiaceæ)* is propagated best by dividing the rhizomes. Ferns may be reared from spores too. In this case, pieces of peat are put into dishes with glass covers after having been soaked with hot water. The lower part of the dishes must always contain water, so that the peat remains sufficiently moist. The spores are sown on the peat. First the prothallus develops and from it, after fertilization, the little fern plants which must be thinned out later on.

The seeds of conifers germinate very slowly, generally speaking. Some kinds want light, others germinate only after a fairly long period of severe cold. The seeds of juniper are reported not to germinate always in the first year. It is best to allow the seeds immediately after the gathering to start germination in moist sand, sawdust or similar materials and to sow them in the second spring. Juniper seeds are said to want a thorough freezing before germinating and it is probable that the same applies to savin seeds.

Calamus *(Acorus Calamus,* L., *Araceæ)* is propagated exclusively by dividing the rhizomes. The fruits only ripen in the hot parts of East Asia, where the plant has come from, whereas they never ripen with us.

Saffron *(Crocus sativus,* L., *Iridaceæ)* is chiefly propagated in autuum through the new bulbs formed. The seeds germinate only in the dark and lie in the soil for several months before starting.

The iris *(Iris florentina,* L., *Iris germanica,* L., and *Iris pallida,* Lam., *Iridaceæ)* can be propagated by dividing the rhizomes and through seeds. These are sown in decayed leaves mixed with sand or in mould and lie a long time before germinating.

The hop *(Humulus Lupulus,* L., *Moraceæ)* is propagated exclusively through pieces of the old rhizome, about 12 to 18 cm. long and with four or five buds. Only female plants are grown. The seeds only germinate in the light.

Hazelwort *(Asarum europæum,* L., *Aristolochiaceæ)* occurs frequently in our woods, so that it would not pay to grow it. The seeds germinate better in the light, but they lie six months before starting.

As to the seeds of *Chenopodium ambrosioides,* L., *Chenopodiaceæ,* no remarks are to be found.

The seeds of love-in-a-mist *(Nigella sativa,* L , *Ranunculaceæ)* germinate in the dark within a few days, whereas they easily become hard in the light. It is advisable, therefore, to cover the seeds well with soil.

The white and black mustard *(Sinapis alba,* L., *Brassica nigra,* L., *Cruciferæ)* germinate completely after 10 days.

Nothing has been published as yet regarding the conditions of germination of the spoonwort seeds *(Cochlearia officinalis,* L., *Cruciferæ),* but it is to be supposed that they germinate easily.

Rearing roses from seeds requires a good deal of gardening experience. The seeds lie in the ground for up to a year until they germinate. It is recommended, on the one hand to sow them already in October after the harvest; on the other, to put them into moist sand, saw-dust, &c., or to let the fruits rot and get mouldy, to wash the seeds out in spring and to sow them then.

The rue (*Ruta graveolens*, L., *Rutaceæ*) is propagated by dividing the rhizomes, through slips and through seeds. The seeds on the market are generally of little value. The germination takes four weeks and is favourably influenced by light. The seeds must be strewn on the surface, rolled in, or pressed down with a plank.

Generally speaking, the seeds of umbelliferæ germinate fairly quickly, but there are exceptions. The influence of the light is favourable in most cases, so that the seeds should not be put too deep. As many of them soon lose the faculty to germinate, the seeds found on the market frequently are not worth cultivating any more or do not germinate at all.

Dill seeds (*Anethum graveolens*, L.) germinate already after a fortnight, especially under the influence of the light or if exposed to changing temperatures.

Angelica seeds (*Archangelica officinalis*, Hoffm.) lose their germinative faculty rather quickly, comparatively speaking[1]).

Caraway seeds (*Carum carvi*, L.) germinate fairly quickly. The germination lasts 21 days.

As to the germination of water-hemlock (*Cicuta virosa*, L.) nothing seems to have been published, so far.

Hemlock seeds (*Conium maculatum*, L.) germinate very slowly and depend much upon the light.

The conditions and duration of the germination of coriander (*Coriandrum sativum*, L.) are the same as for caraway.

Fennel seeds (*Fœniculum vulgare*, G.) start germinating quickly, the whole process being completed after a fortnight.

Regarding lovage seeds (*Levisticum officinale*, Koch) the conditions are the same as with angelica. Bought seeds had almost entirely lost their germinative faculty. As it decreases so rapidly, it is best to sow the seeds soon after having gathered them, in autumn.

The water-fennel (*Oenanthe aquatica*, Lam.) is propagated either through runners from the root-stock, put in the mud of drained ponds, or through seeds, sown in very moist places, immediately after having ripened. Gentner has not been able to find any notice concerning the conditions of germination.

The seeds of master-wort (*Peucedanum Ostruthium*, Koch) are sown soon after the harvest, the same as angelica and lovage seeds. No further particulars seem to be known.

Parsley seeds (*Petroselinum sativum*, Hoffm.) generally germinate completely after a fortnight.

Anise seeds (*Pimpinella Anisum*, L.) and probably those of *Pimpinella magna*, L., and *Pimpinella saxifraga*, L., have a quick normal germination.

Marsh-rosemary (*Ledum palustre*, L., *Ericaceæ*) only germinates in the light, but is scarcely cultivated, as it grows in profusion in parts of the North-German moors.

A good many *Labiatæ* are generally not propagated by seeds, but through runners or slips, or by dividing the root-stocks *e. g.* hyssop, lavender, balm-mint, peppermint and spearmint. The seeds germinate rather slowly. Many of the native *Labiatæ* require light for germinating and are favourably influenced by a cool temperature, so that it is advisable to strew the seeds on the surface. A considerably part of the seeds on the

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[1]) Comp. B. Pater, *Pharm. Post* **1916**; *Report* October **1917**, 110.

market is worthless. Hyssop seeds (*Hyssopus officinalis*, L.) germinate 4 or 5 weeks after having been sown. The same applies to the seeds of lavender (*Lavandula vera*, DC.), balm-mint (*Melissa officinalis*, L.), peppermint (*Mentha piperita*, L.), spearmint (*Mentha crispa*), marjoram (*Origanum Majorana*, L.), sage (*Salvia officinalis*, L.), thyme (*Thymus vulgaris*, L.) and rosemary (*Rosmarinus officinalis*, L.). It is indicated that the germination of these plants lasts 21 days. The conditions are likely to be identical for *Monarda didyma*, L., and basil (*Ocimum Basilicum*, L.), although there are no data to hand. Wild marjoram (*Origanum vulgare*, L.) germinates more slowly than the true marjoram, and wild thyme (*Thymus Serpillum*, L.), more slowly than real thyme.

Valerian (*Valeriana officinalis*, L., *Valerianaceæ*) is propagated partly by dividing the root-stocks, partly through seeds. These are sparsely sown on the surface, in spring, and rolled in. Sometimes, they are sown in frames, when the seedlings must be transplanted, as soon as they are big enough. The seeds germinate best in the presence of sufficient light and moisture. The act of germinating is rather slow and the seeds on the market often leave much to be desired.

The *compositæ* seeds generally distinguish themselves by germinating readily and in a normal way. Yarrow (*Achillea millefolium*, L.), wormwood (*Artemisia Absinthium*, L.), tarragon (*Artemisia Dracunculus*, L.) and mugwort (*Artemisia vulgaris*, L.) seeds have been found to require only 10 days for their germination.

All *compositæ* seeds are more or less favourably influenced by light in their germination, so that they ought to be sown on the surface and pressed down. An experiment made with corn chamomile (*Matricaria Chamomilla*, L.) had the following result: 60 per cent. of the seeds germinated within 10 days, 20 per cent. were still unaltered after that period and another 20 per cent. had rotted.

There are no data available as to the germination of chamomile (*Anthemis nobilis*, L.) and tansy seeds (*Tanacetum vulgare*, L.), but it may be supposed that it takes place quickly and in a normal way.

Diseases of plants yielding essential oils.—Now and then one finds something on this subject in trade-journals[1]), mostly with regard to damage caused by fungi. This time, we are in a position to report on an article by Th. Sabalitschka[2]), in which not only these are taken into consideration, but also insect pests.

The "sclerotic disease" of the caraway plant is caused by a fungus. In the beginning, it becomes noticeable through white or coloured spots on leaves and stalks; later on hard black lumps, white inside, form on and in the stalks. The disease is caused by a fungus, *Sclerotinia Libertiana*, Fekl., which also attacks other cultivated plants, such as ordinary and runner beans. It can be avoided by carefully destroying the fungi on the seeds and cultivating the plants on soil that is not excessively moist. The snowy-white agglomerations of the spores of *Pernospora nivea*, the "false mildew", form pale spots on the leaves, leading to decay. Another fungus, *Protomyces magrosporus*, Ung., causes on the leaf-stems and on the stalks pale weals, 1 to 5 mm. long, which dry up later on, when the leaves gradually become yellow and fade. Similar diseases are treated best by spraying with so-called "Bordeaux solution". Glasslike excrescences on stalks, leaf-stems and leaves, sometimes on the umbels and the ovaries are caused by two allied fungi, *Synchytrium aureum*, Schroet., and *Urophlyctis Kriegeriana*, Magn. Both fungi are not common and do not cause any considerable damage.

The caterpillars of the swallow-tail butterfly (*Papilio machaon*) and the silver-Y-moth (*Plusia Gamma*) are rather fond of the caraway leaves and shoots. Both are naked and

[1]) Comp. *Report* October **1915**, 64. — [2]) *Deutsche Parf. Ztg.* **4** (1918), 46.

can best be killed by spraying with a quassia wood decoction. The larvæ of the fly *Chlorops glabra*, Meig., are probably responsible for the black colour and the rotting of the leaves at the bottom, followed by the withering of the heart-leaves and their slow decay. The chrysalises of this fly are found in the soil near such plants. The greatest harm is done to caraway plants by the vivacious small caterpillars of the caraway moth, *Depressaria nervosa*, Haw., and Blunt's flat-body, *D. depressella*, Hb., which eat the flowers, thus preventing fructification. The flowerets and young fruits are pulled together with a fine web. Other umbelliferæ are likewise attacked, such as the carrot. The caterpillars of the former pupate inside the stalks, so that they can be destroyed by removing and burning the stalks attacked. Otherwise, it is to be recommended to thrash the plants quickly and burn the straw. The caterpillars of *Depressaria depressella*, however, form their chrysalises in the soil.

Sometimes it is to be observed that the flowerets are transformed into small whitish green leaves, which is due to a mite of the *Eriophes*[1]) family. Galls at the ends of the chief pedicels are inhabited by the red larvæ of the gall-gnat *Lasioptera carophila*, F. Lw. The small fruits can likewise be transformed into vesicular galls by the larvæ of the gall-gnat *Schizomya Pimpinellæ*.

The caraway roots are attacked by the larvæ of *Bibio hortulanus*, L. This pest can be kept within bounds by rolling the ground in April.

Furthermore, *Heterodera radicicola*, Greeff, invisible to the naked eye, may inhabit the roots and cause small swellings.

Whereas the insect pests which attack caraway are equally common with fennel, one scarcely ever finds its leaves and stalks attacked by fungi, in any case not by those occuring on caraway. Only in France, a kind of rust, *Aecidium Foeniculi*, Cast., has been observed. It forms on the fennel leaves and stalks, sometimes even on the fruits, yellowish places with swellings containing a yellow powder. As to parasites of a higher order, the ill-famed lesser dodder, *Cuscuta Epithymum*, is occasionally encountered on fennel plants. Its yellowish or reddish, thin, leafless stems with their clusters of tiny flowers creep round the fennel stalks and, using up all the nourishment for themselves, eventually kill the whole plant. The best preventive is to use seeds which have been carefully freed from dodder seeds. In order to destroy the parasite once it is there, the places infected ought to be mown and covered with chaff or such like material, about 10 cm. high. This must then be stamped firmly down. Another method consists in putting on a layer of chaff, 20 to 30 cm. high, moistening with petroleum and burning it. A further remedy is to cut the infected plants with a sickle and to burn them, and then to spray the places thoroughly with a 15 per cent. ferrous sulphate solution.

Leaf-lice and thrips suck on the leaves and young shoots of fennel plants. The former, *Aphis Genistæ*, Scop., and *A. Capreæ*, Fb., secrete a colourless, sticky, sweet liquid, which falls on the lower parts of the plants and forms the so-called honey-dew. There are winged and wingless forms of either. In order to avoid considerable damage, the leaf-lice colonies must be destroyed with so-called "Nessler's tincture" (a solution of soft soap in water with fusel oil and carbolic acid), quassia extract or an emulsion of petroleum and tobacco dust.

The thrips (*Thrips physopus*, L.) can be killed in a similar way.

Fennel may suffer from caterpillars too, such as those of the swallow-tail butterfly, the dot (*Mamestra persicariæ*, L.) and *Boarmia selenaria*, Hb. The caterpillar of the dot may become dangerous, if occurring in masses, the best remedy being to gather them. The caraway moth sometimes destroys the fennel flowers, and the larvæ of

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[1]) *Eryphyes?*

Lasioptera carophila, F. Lw., or of *Schizomyia Pimpinellæ* may form similar galls as on the caraway umbels.

The fennel roots can be destroyed by the dark violet mycelium of *Rhizoctonia violacea*. As this disease spreads, bare spots form in the fields. It is recommended to dig such places over, and to burn the infected plants. The roots are further attacked by the larvæ of *Bibio hortulanus*, L.

Caraway and fennel may also be attacked by the enemies of other cultivated plants, such as mice, the larvæ of the cockchafer, &c.

Sabalitschka likewise discusses the fungi and insects which attack roses and some other essential oil plants. As to the former, we beg to refer to a previous publication[1]).

We have not encountered in our rose-fields, so far, the gall gnat *Dasyneura rosarum*, Hardy, mentioned by Sabalitschka. It lays its eggs near the main veins of the rose leaves, before these are fully developed. They then do not grow any more but form a sort of pod, inhabited by numerous larvæ. The gnat is reddish brown, 1.5 mm. long, and has black stripes across the abdomen. The larvæ are 2 mm. long, orange yellow and pupate in the earth.

Sabalitschka is wrong in saying that *Athalia rosæ* is found on roses, for it never attacks them, but only *Lycopus europæus, Scutellaria galericulata*, &c. The German name *"Rosenbürsthornwespe"*, by the way, does not belong to it, but to *Hylotoma (Arge) rosæ*, L., because of the antlers of the males being brushlike.

As to beetles, Sabalitschka[2]) mentions *Phyllopertha horticola*, L., and *Cetonia aurata*, L. He states that the larvæ of the latter live, *e. g.*, in the nests of the red ant. This is a mistake, found in old books on insects, it is true, but that is due to a confusion with *Potosia (Cetonia) cuprea*, F.

Finally, the author mentions some fungi living on hyacinths, violets, mignonette, lilac and peppermint. Having discussed the diseases of these plants in the article quoted above, we need not go into details again.

Phyto-physiological Notes.

Fresh knowledge concerning assimilation. — We have hitherto known but little as to the chemical changes, taking place during the process of assimilation, which is of such fundamental importance for the life of the plants. A. Meyer[3]) has now published a fresh contribution. On account of his observations, he supposes that, while the chloroplast prepares hydrocarbons from carbonic acid and water during the process of assimilation, a secretion forms in it that separates in the shape of drops. It seems to be identical with all the chloroplasts and he presumes that it is a direct product of the assimilating process, the same as the hydrocarbons. One is there led to regard as similar secretions the large drops occuring in every mesophyll cell of evergreen leaves, secretions which have formed owing to the assimilative action of the chloroplasts during a long period and which have been deposited in the cytoplasma. Such drops have often been seen and investigated.

These drops can easily be distinguished microchemically from drops of fat. If treated with ammoniated potash lye, they do not become crystalline, as fat drops would, and treated with fuming nitric acid, they become oily after a few days, whereas fat drops would remain clear. The drops used for these reactions were taken from fairly old, yet completely green leaves. They further behaved as follows: insoluble in water, soluble

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[1]) Comp. *Report* October **1915**, 67. — [2]) *Deutsche Parf.-Ztg.* **4** (1918), 109. — [3]) *Berichte d. deutsch. Botan. Ges.* **35** (1917), 586, 674. As per a special copy, kindly sent us.

in alcohol 95 per cent., insoluble in alcohol 40 per cent., soluble in ether, insoluble in glacial acetic acid + 15 per cent. water, but readily soluble in pure glacial acetic acid, coloured brown by osmic acid and black by ammoniated nitrate of silver. The secretion is lighter than water and evaporates at 120°.

Meyer tried with succes to obtain a substance of the same properties as the secretion formed during the assimilative process, by heating powdered leaves and then by extracting with ether. He presumes that the leaf-aldehyde, discovered by Curtius, Reinke and Franzen[1]) in the green parts of plants, and which they considered to be α,β-hexylene aldehyde, is the chief component of the secretion. The general occurrence of the hexylene aldehyde in all the leaves examined corresponds with the general presence of the secretion in the chloroplasts of the leaves. The chloroplasts of etiolated leaves do not contain any secretion due to assimilation. This is why no aldehyde can be obtained from etiolated germs. It is to be presumed that other substances participate in building up the secretion, such as hexylenic acid and its homologues, the higher homologues of the α,β-hexylene aldehyde and hexylene alcohol, bodies obtained by Curtius and Franzen on distilling leaves with steam.

Up to a certain degree, the presence of a hexylenic alcohol in Japanese peppermint oil, as observed by us, may be looked upon as a confirmation of Meyer's results. It is true, however, that we found an alcohol of a somewhat different structure from that which would correspond to a α,β-hexylene aldehyde, for as we stated on page 39 of this *Report*, it is a β,γ-hexylene alcohol.

The importance of the epidermis for the assimilative process in plants. — How and where the different plant substances are formed and for what purpose, is an unsolved question still in most of the cases. As far as essential oils are concerned, they are considered sometimes as a protection against excessive radiation of heat during the night, against excessive evaporation in day-time, against being eaten by animals, as an attraction for insects; sometimes as final products of the assimilation and as useless ballast. Be it as it may, the place where they where formed was not known, only the view that no chemical process of building up or down took place in the epidermis was sustained by a good many. This is not the case, however, as A. Tschirch[2]) explains in a treatise on the localization of chemical work in the plant. About 40 years ago, it was still taught that the epidermis of plants was void of substance and if slides were made, they seemed to confirm this view. Colourless protoplasm or, in the case of red leaves, a red solution was all that could be seen. The chemical process of building up, it was said, was only carried out by the plasma of the cells.

Already a year ago, Tschirch has shown, that there is a certain membranous layer right through the whole plant, that has no direct contact with the plasma but is fit to be chemically active and that this membranous layer is either the intercellular substance itself, or originates from it or is the direct continuation of it.

As to the epidermis, it is a well-known fact that it may contain representatives of two important classes of bodies; *viz.*, alcaloids and glucosides. This conviction has only slowly gained ground. When compiling the *Mentha* and *Conium* species for the anatomical atlas, which he edited together with Oesterle, Tschirch observed that the material prepared with alcohol showed sphæro-crystals in the epidermis, and only there. It was easy to comprobate that such crystals were also to be found in many other plants under the

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[1]) Comp. *Reports* April **1911**, 160; October **1912**, 138. — [2]) *Berichte d. deutsch. pharm. Ges.* **27** (1917), 447; *Schweiz. Apotheker-Ztg.* **56** (1918), 162, 173, 175.

same circumstances, *i. e.* preserving in alcohol. This phenomenon is generally explained by that one has to deal with the glucoside hesperidine[1]), originally dissolved in the protoplasma, but forced by the alcohol to crystallize. When studying the plants containing alcaloids, Tschirch's attention had been attracted by the fact that with them too the bases are localized in the epidermis. He then said in his anatomical atlas: "Just in the epidermis we find many active bodies and especially the alcaloids seem to prefer the epidermis". He thus proclaimed the opposite of the thesis considered as a kind of dogma: The epidermis has merely the function of a periphere water-tissue and forms a water-cover.

In the course of several years, the examples increased considerably in number. As to alcaloids, Tschirch's thesis was confirmed for nearly every plant examined. Almost the same holds good for the glucosides. They likewise distinctly prefer the epidermis, not only the hesperidine, but it is still more the case with a third group of bodies, the tannides, as quite recently Dekker's investigations have shown, who by introducing the branches into a potassium acid chromate solution precipitated the tanning substances *in loco*, thus avoiding any misunderstanding.

The results of the various investigations point to a severe division of labour in the chemical work. Alcaloids, glucosides and tannides are formed as little in the places of assimilation as in the ducts, these being carefully kept free from such substances.

A certain chemical antagonism corresponds with this topographic-anatomical one: the acylic compounds, the hydrocarbons and the albumens are formed and conveyed in tissues absolutely free from cyclic compounds. These, such as alcaloids, glucosides with cyclic aglucone, such as tannides, are found in other tissues, in the epidermis and the immediate vicinity of the fascicles. They have in no case been conveyed to these places, but have been formed there. The cells and tissues in question must therefore have the power of closing the ring of the originally acyclic system, for in the assimilative process only acyclic carbon compounds form and only such wander. As soon as the ring is closed, a terminal point of a range has been reached. The cleavage of the ring and with it the retrocession into the assimilative process is very rare in any case. It happens only under quite exceptional circumstances, most likely only in case of extreme need.

The typical closing of a ring, through which an acyclic system becomes cyclic, is shown us in the transformation of a hexose, known to be acyclic, into a cyclic inosite. Also in the case of the alcaloids, the closing of rings is to be supposed. It is the same with tannides, for the prototannides are aromatic phenoles, which we likewise can imagine as having formed from hexoses by the closing of the ring, connected with a reduction or with water being split off. It is true, that the closing of the ring does not always lead to tannides, sometimes the sweet taste is retained, such as with phloroglucine and the product of its reduction; *viz.*, phoroglucite, corresponding to inosite. With alcaloids as well as with tannides, it is to be observed that they combine with saccharides, and especially with hexoses, to form glucosides. The alcaloids do it rather seldom; but the tannides, fairly frequently. The non-tannidish glucosides form a great class. The constitution of the aglucone of many glucosides has not been determined as yet. That of the hesperidine is known. It is called hesperitine and Power and Tutin have recognized it as *2,4,6*-trihydroxyphenyl-*3*-hydroxy-*4*-methoxystyrylketone. In addition to alcaloids, tannides and glucosides, red colouring matter occurs in the epidermis of leaves. The anthocyane, for example, is also a cyclic compound, derived from flavonole, as Willstätter has shown.

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[1]) Regarding hesperidine as a pathological product of the peppermint plant, comp. *Report* April **1915**, 32.

All these compounds, found in the plasm, probably also form in it. As a rule, but little plasma is to be found in the cells of the epidermis and we may therefore look upon their content as being in the main a colloidal solution, in which under the influence of enzymes all reactions can take place as energetically as in the plasma. Especially these enzymes of the plasma seem to be endowed with the power of closing the ring and enlarging it. As manuring, *i. e.* the supply of anorganic nutriment, does not raise the alcaloid content considerably, according to the experiments made up to now, it is probable that the metallions do not take part in the closing of the ring. They evidently act an important part in the formation of aliphatic substances, as is indicated by the comparatively high content of ashes in the leaves, a fact which has not been sufficiently apprecicated as yet. That nitrogenous manure will often raise the content of alcaloids to double the quantity, *e. g.* with belladonna, is due to the general increase of the assimilation of nitrogen through which more by-products will naturally be formed.

Tschirch explains that, as only aliphatic substances can form in the assimilative process and only they can wander, the closing of the ring does not take place in the specific assimilative tissue or the conveying system, but in the epidermis and in the tissues surrounding the ducts. The useless "splinters" are cleared out of the proper tracks, "washed ashore", as Tschirch calls it, and consolidated and fixed in the non-conducting tissues by the closing of the ring.

Tschirch denies that alcaloids, glucosides and colouring matter have the power of moving about, the same as he denied it for the secretions, in opposition to the view of the French scientists[1]), who suppose that there is a moving from organ to organ, for instance with the components of the essential oils. They remain on the spot, where they have been formed, or are only quite exceptionally, in case of extreme need, conveyed back into the assimilative process. Young tissues being often richer in alcaloids than old ones, and young shoots or germs richer than the seeds, is not caused by the alcaloids moving to these centres of assimilation, but by the "washing ashore" being specially intense there. Tschirch does not go further into the question, as to whether the plant has another biological aim in the agglomeration of alcaloids, glucosides and colouring matter in certain places but the simple removal of final products of the assimilative process.

He points out that the wax-covers as well as the cuticula, which both behave like secretions of the membrane, apparently only contain acyclic compounds, such as cerotinic acid, myricylic alcohol and cerylic alcohol. In addition to them, we find in the cuticula aliphatic hydrocarbons (paraffins), which pass over when leaves and petals are distilled in large quantities and then crystallize out of the distillate, such as the stearopten of otto of roses. We have to suppose that these aliphatic substances are formed in the outer membrane of the epidermis cells, for they never occur in the contents of the epidermis cells.

The more we penetrate into the constitution of vegetable matter, the more we recognize that the means with which the plant works are really very simple and that the reactions can be reduced to a very few types. As an example, Tschirch mentions the well-known fact that the aliphatic system contained in geraniol closes to form the hydroaromatic terpene nucleus and leads to the aromatic cymene with its many derivatives.

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[1]) Tschirch apparently means the publications of E. Charabot, A. Hébert, G. Laloue and Roure-Bertrand Fils, discussed in our *Reports*. Comp. *Reports* April **1900**, 50, 51; April **1905**, 89, 90, 91; October **1905**, 89; April **1906**, 104; October **1906**, 106; April **1907**, 126; October **1908**, 162, 163.

He further points out the close chemical relation between vegetable substances of similar pharmacological action, mentioning among others the saponin drugs, the mustard oil drugs and the hydrocyanic acid drugs, which constitute families of the natural order.

The frequent occurrence of the hexacyclic ring explains itself quite naturally, according to Tschirch, from the hexataxis of the hexoses, the most frequent form in which sugar occurs in plants. As to the equally frequent presence of the methoxyl group, he traces it back to the occurrence of formaldehyde among the products of assimilation. The reactions in the organism of the plant should be supposed to take place under the influence of synaptases and cyclokleiases (coupling or ring-closing enzymes). On the other side, there would be the resolution into smaller particles, under the influence of schizases, *i. e.* cleaving ferments. The established fact that minute quantities of enzymes may bring about most energetic reactions even at the ordinary temperature. may without any hesitation be claimed for the explanation of the proceedings in the laboratory of the plant cell, proceedings that we can understand all the better, now the chemical action has been localized and shown to be based upon an extensive division of labour.

Smells of mushrooms. — On pages 100/102 of our *Report* of April/October **1916**, we discussed E. Herrmann's[1]) treatise on smells of mushrooms. The following details are taken from a further[2]) publication of his, full of details.

A smell of anise is found, in addition to the mushrooms previously mentioned, in *Clitocybe alutacea, C. obsoleta, C. suaveolens, C. fragrans* and *Lentinus cornucopioides,* the last-named being found on rotting tree trunks of pine forests. The same smell is met with, in a higher or a lower degree, in *Psalliota perrara, P. pratensis, Fomes odora* and *Tramates suaveolens,* the latter two growing on trees.

The smell of fennel is not frequent. We find it with *Polyporus squamosus* and *Fomes ribis.* Old specimens of *Clitocybe nebularis* have a mixture of fennel odour and an obtrusive, almost repugnantly sweet smell.

Calodon compactus smells of cinnamon.

An odour of melilot is to be noticed with *Hydnum graveolens.*

Octaviana asterospora, a small ball-shaped fungus looking like truffles, possesses a smell of basil.

As to a smell of onions, we find it with a good many kinds of *Marasmius,* such as *M. porreus, M. alliaceus* and *M. perforans. Telephora palmata,* the little tuberous *Gautieria graveolens, Hymenogaster Klotzschii,* the brownish yellow *Rhizopogon luteolus,* the reddish *R. rubescens* and *Melanogaster ambiguus.*

The poisonous common earth-ball, *Scleroderma vulgare,* when dried, *Polyporus benzoinus, P. fumosus, P. melanopus* and *P. vaporaria* have a spicy smell.

Like fruit generally speaking smell *Tricholoma caligatum* and *T. chrysenterum.*

Hydnum Schiedermayri, a dangerous parasite on apple-trees, smells of apples, when fresh; in a dry state it smells repulsive.

A smell of pears occurs in *Inocybe scabra, J. pyriodora* and *Naucoria suavis.*

Cratarellus lutescens reminds one of the smell of strawberries.

Limacium agathosmum and *L. eburneum* smell of bitter almonds.

Tricholoma calathum and *Naucoria cucumis* smell of fresh cucumbers.

A smell of flour is encountered with *Nyctalis asterophora, Hygrophorus metapodius, Phlegmacium emollitum, Pholiota præcox, Ph. marginata, Ph. phalerata, Ph. unicolor, Lepiota*

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[1]) *Pharm. Zentralh.* **56** (1915), 555. — [2]) *Ibidem* **59** (1918), 1, 7, 19.

guttata and numerous kinds of *Tricholoma* which it would lead too far to enumerate. The same applies to the *Clitocybe* group, a good many of which smell of flour, although often but faintly. A few *Collybiæ, viz., C. coracina, C. ozes, C. misera* and *C. nitellina,* further the tiny *Omphaliæ maura, atropuncta, umbratalis, plumbea* and *grisea* and finally *Mycena pelliculosa, Pleurotus cornucopioides, P. lignitalis, P. fimbriatus, P. geogenius* and *Calodon hybridus* may be mentioned as having a similar odour.

According to Ricken, *Inocybe frumentacea,* smells of cereals; others say of whisky. It is said to be very poisonous.

Clitocybe absinthiaca smells of wormwood.

It is not always easy to define the odours by comparing them with those of well-known things in nature. Some mushrooms have quite a special smell of their own and that of others is often not definite enough to be called otherwise than agreeable, sharp or repulsive.

Cantharellus olidus, Lepiota seminuda and *Collybia succinea* smell agreeably.

A repulsive smell characterizes *Flammula amara, Fl. sapinea, Entoloma lividum, Lepiota Friesii, L. cristata, Tricholoma album, T. grammopodium* and *Thelephora fastidiosa.*

A repulsively sweet smell is typical for the *Inocybe* species. *Entoloma madidum* has a similar odour. *Amanita phalloides* smells peculiarly sweetish.

Clitocybe inversa, Polyporus adustus, Polystictus versicolor and *Trametes gibbosa* have a sourish smell.

An earthy smell is found in *Paxillus involutus, P. helomorphus* and *Inocybe dulcamara,* whereas a fusty one occurs in *Myxacium mucosum, Telamonia hinnulea,* the panther-cap *(Amanita pantherina)* and *Thelephora cristata.*

Tricholoma virgatum, T. vaccinum and *T. sordidum* smell earthy, but in a disagreeable way.

The smell of *Polyporus chioneus* is sharp, that of *P. stipticus* is nauseous.

Hygrophorus nitratus, Mycena alcalina, M. amoniaca, M. leptocephala and *Lepiota meleagris* have a pungent smell of ammonia, the last named considerably less than the others.

The odour of *Entoloma nidorosum* reminds one of nitric acid.

Rather uncommon is the smell of cod-liver oil, as found in *Telamonia flabella* and *Collybia atrata.*

A fishy smell occurs in *Collybia distorta, C. conigena* and *Lactaria volema,* in this, however, only when it is old or dried. In a fresh state, it is completely odourless.

Tricholoma mirabile, T. goniospermum and *T. putidum* smell like mouldy flour, whereas *T. semitale* has a rancid odour, the same as *Clitocybe nimbata, C. ditopus, C. vibecina, Collybia rancida, C. megalopus, Mycena olida, M. viscosa* and *M. lasiosperma.*

There is a smell of bugs in *Boletus pachypus,* whereas the strongly smelling *Limacium cossum* reminds one of the goat moth *(Cossus ligniperda).*

The smell of radish is rather widely spread, for it occurs in *Hebeloma firmum, H. fastibile, H. sinapizans, H. elatum, H. diffractum, Inoloma violaceocinereum, I. argentatum, I. tophaceum, Dermocybe raphanoides, D. colymbadina, D. cinnabarina, D. sanguinea, Hydrocybe armeniaca, Pholiota squarrosa, Ph. aurivella, Ph. flammans, Naucoria lugubris, N. festiva, Lepiota medullata, Mycena pura, M. denticulata, M. Renati* and *Hysterangium clathroides.*

Tricholoma sulphureum, T. inamœnum, T. lascivum and *Clitocybe amarella* smell of coal-gas.

As to the relations between smell and edibility, it may be said, generally speaking, that mushrooms with an anise, fennel, fruit, strawberry and cucumber smell are edible, but there are also mushrooms which smell agreeably and are unfit for being eaten.

Mushrooms with a smell of onion are mostly good for flavouring, such with a smell of almonds are edible, excepting *Russula fœtens*. The odour of flour generally indicates edibility, exceptions being *Tricholoma sejunctum* and *Inocybe frumentacea*.

Fungi with a repulsive sweet odour or which smell of ammonia, cod-liver oil, bugs and potatoes are unfit to be eaten. The smell is no sure criterion of general validity as to whether a mushroom is edible or not, but it is quite important for determining the species and facilitates the differentiation of doubles.

On page 123 of our *Report* of October **1917**, we discussed a note of R. Kobert[1]) according to which the *Psalliota* varieties can be separated into an anise and a bitter almond group. He[2]) now reverts to this question. Pannwitz[3]) thinks that round Stuttgart all the *Psalliotæ* smell of hydrocyanic acid, W. Obermeyer says it is only the case with *P. campestris* and *arvensis*, whereas *P. vaporina* smells remarkably strongly of anise and all the other kinds are odourless.

In most of the books on fungi, the smell of the stinkhorn is described as repulsive, reminding one of carrion. M. Wegner's[4]) opinion is that it does not smell so disagreeably. He would call it "obtrusively sweetish" similar to privet blossom, which view is confirmed by Fischer in a treatise on the *Phallineæ*, who likewise calls it sickly sweetish, recalling mustard seed oil[5]).

As to an abnormal crystalline secretion, called hyssopin, in hyssop plants attacked by fungi, see page 32 of this *Report*.

The influence of the mandelic acid nitrile on germinating plants. — Contrary to the essential componants of plants (fats, sugar, proteins) the accidental ones (glucosides, alcaloids, colouring matter, aromatics, &c.) have not been investigated as yet with regard to their biological value. In consequence, G. Ciamician and C. Ravenna[6]) endeavoured to investigate the influence of such bodies on the development of the plant. First the action of mandelic acid nitrile on indian corn and beans was studied. It was found that a 1 per cent. solution prevented germination, whereas an equivalent solution of amygdalin did not have any such effect. If the plants, especially beans, are allowed to develop in a solution of mandelic acid nitrile, they are distinctly different from those grown in water or a food solution. The roots are less developed and the plants are not so high, but bushier and hardier with regard to the influences of winter. The plants contained neither prussic acid nor benzaldehyde. Further developed plants, which have not been accustomed to the poison, die quickly if treated with mandelic acid nitrile, as mentioned before. Prussic acid also handicaps the germination. The authors further investigated the action of strychnine, nicotine, coffeine and morphium.

Physiological and Pharmacological Notes.

New notes on the theory of smelling. — Two treatises by A. Durand[7]) entitled *"Sur l'olfaction"* and *"Corrélation entre les phénomènes de condensation et d'olfaction"*, deal with this matter. The author gained the conviction that the particles of aromatic

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[1]) *Chem.-Ztg.* **41** (1917), 61. — [2]) *Ibidem* p. 755. = [3]) *Ibidem* p. 461. — [4]) *Pharm. Zentralh.* **58** (1918), 49. — [5]) A. Engler and K. Prantl, *Die natürlichen Pflanzenfamilien* (The Natural Plant Families), part I, division 1**, p. 292, Leipzig 1900. — [6]) *Atti R. Accad. dei Lincei, Roma* (5) **26**, I. (1917), 3; *Chem. Zentralbl.* **1917**, II. 233. — [7]) *Compt. rend.* **166** (1918), 129, 532.

matter dispersed in the air have the power of condensing water vapour. If air, after having been filtrated through cotton wool, is passed over musk or camphor, it results that, thus laden with aromatic matter, it has acquired the property of forming a fine mist in a Coulier's flask by relaxing the tension.

According to Durand, the physical conditions for smelling are: —

1. a certain amount of moisture in the air,
2. condensation of the moisture of the air on the odorous particles,
3. separation of the moisture during the act of breathing in (phenomenon of relaxation).

The aromatics act only if surrounded by moisture.

The condensation explains the great difference in the intensity of smell on various days, as well as the observation that the smells are more penetrating during the moister times of the day, *i. e.* at daybreak or at nightfall, than in broad daylight.

H. Henning[1]) *published a mostly theoretical article on the modification of an odour in different concentrations.* — He mentions as being specially worthy of note that concentrated anethol smells of alcohol, diluted like anise; concentrated ionone somewhat of herbs, diluted like violets, and that concentrated methyl anthranilate does not smell in the same way like oranges, as the dilute substance. Given the nature of Henning's communications, they do not lend themselves to a condensed reproduction.

The same author[2]) published an article on mixed odours. If the odour of a mixture is compared with that of the isolated components, it is to be noticed that no foundamentally new smell has been produced, as we find it with colours, where on the one side complementary colours give rise to an unshaded grey and on the other side dissimilar colours unite to form new shades. In a mixture of several aromatics, one only finds a more or less pronounced union of the smells of the ingredients. In no case does the mixture produce an astonishing effect, dissimilar from the ingredients: the numerous aromas of a chemist's or a flower shop will always represent the pharmaceutical goods or the flowers which are there at the time, but never give us the sensation of the smell of a grocer's or a cheesemonger's shop. A distinctive smell can therefore only be obtained, if the corresponding aromatic itself be chosen, but not through mixing other aromatics. Quite different from colours, the combination of smells rather seems to ressemble that of musical tones, as the different tones combine to form a unity, the accord, and as in the accord they all arrange themselves to one sound. Only, there is no analogy with the firm relations of tones, such as the third, the octave, &c. But there are other analogies instead: as a weaker tone may be suppressed by the others of the accord, so that it is not noticed at all, a component of a smelling mixture may be suppressed altogether or temporarily.

As the union of sounds is more intense in some accords, such as the octaves, than in others, *e. g.* the seconds, so is the case with smells. If we mix couples of aromatics of similar smell, such as vanillin and heliotropin, we find it difficult to discern the one or the other, but dissimilar smells, such as of thymol and pyridine, form a looser union, which may even split by itself into the components.

The author further discusses the tremendous influence of experience on the production of a uniform impression, mentions the difficulties met with when trying to find out with the nose the components of complicated mixtures and finally touches on the imaginations produced by mixtures, with which we are unacquainted.

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[1]) *Deutsche Parf.-Ztg.* **3** (1917), 151. — [2]) *Ibidem* 162.

A new olfactometer. — In order to measure smells, a so-called olfactometer has been constructed, and we described at the time[1]) the type recommended by Zwaardemaker. C. van Dam[2]) has devised a different one. He mixes any quantity of odorous matter with 10 grams of melted paraffin (m. p. 60°) and forms out of this mass sticks 3.5 cm. long and 0.6 cm. wide. They are fixed up in small copper tubes, which can be screwed on a copper stick 10 cm. long. The olfactometer is composed of a cilindrical glass air-chamber 1.5 m. wide and 16 cm. long, into which at the one end a glass-tube 8 cm. long and 0.6 cm. wide projects 6 cm. The paraffin sticks are placed in this tube. At a right angle to the axis of the air-chamber, there is another glass-tube 8 cm. in length and 0.6 cm. in width, at which one smells. The imbued paraffin stick is introduced into the tube first mentioned and pushed in carefully until, at the other tube, one distinctly perceives the smell. The distance between the paraffin stick and the inner opening of the introductory tube corresponds to the intensity of smell.

C. van Dam[3]) tried, with the aid of this olfactometer to determine the adsorptive power of various materials (gold, silver, platinum, iron, wood, ebonite, glass, quartz, bone [ivory?], &c.) with regard to certain volatile liquids, such as ionone, eugenol, acetophenone, nitrobenzene, and so on. He placed one drop of the liquid, by means of a thin stick, on the bottom of a cylindrical flask, which was then closed. As soon as the smell had spread uniformly, a cylinder of the material to be tested was introduced for one minute into the flask and then placed into the olfactometer. The results differed, although with some of the substances a relation between absorptive power and chemical constitution was noticeable. It was impossible, however, to determine them quantitively.

J. H. Kremer[4]) studied the same subject in another way. He showed, with the aid of a spectroscopic method, that a liquid containing a lipoid, suspended lecithin, or a fatty animal tissue in Ringer's solution, adsorbed more odorous substance than water, if air saturated with some aromatic body, such as pyridine or camphor, was passed through.

It is well known that *essential oils are used as a protection against insects,* especially gnats. J. Hamerton[5]) recommends, as especially effective against flies, a mixture of 1 part pyridin, 1/2 part thymol, 5 parts safrole, 5 parts birch-tar oil and 88 1/2 parts spermaceti oil. Birch-tar oil and safrole shall hide the smell of the pyridin and, together with thymol, delay volatilization. The mixture does not irritate the skin and is just as efficacious with people as with horses. It must be applied in a thin layer to the temples, the forehead, the ears and the back of the hands.

As to the disinfecting power of the oil of cryptomeria wood, see p. 21.

The injection of turpentine (oil?) in the treatment of wounds is discussed on p. 45 of this *Report.*

H. Thierfelder and E. Schempp[6]) *report how phenylethylic alcohol is affected in the human body and in dogs.* — It was possible to isolate phenylacetylglutamin and its urea com-

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[1]) Comp. *Report* October **1904**, 104. — [2]) *Arch. Néerland. Physiol.* **1** (1917), 660; *Journ. chem. Soc.* **112** (1917), I. 606. — [3]) *Arch. Néerland. Physiol.* **1** (1917), 666; *Journ. chem. Soc.* **112** (1917), I. 607. — [4]) *Arch. Néerland. Physiol.* **1** (1917), 715; *Journ. chem. Soc.* **112** (1917), I. 607. — [5]) *Pharmaceutical Journ.* **95** (1915), 134. — [6]) *Pflügers Arch. d. Physiol.* **167** (1917), 280; *Chem. Zentralbl.* **1917**, II. 238.

pounds from human urine. Experiments with dogs showed that phenylacetic acid had been formed by oxidation.

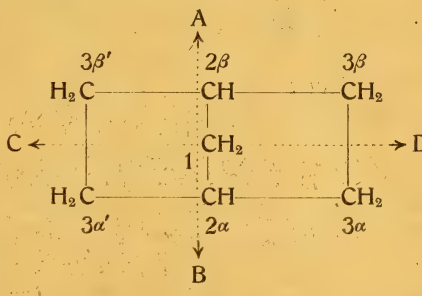
As to the poisonous action of thymol, see p. 70 of this *Report*.

The preserving action of thymol with regard to urine is mentioned on p. 71.

Chemical Notes.

Chemical research has at different times already dealt with the *nomenclature of bi- and polycyclic compounds*, a satisfactory solution, however, has not been found hitherto[1]). In the opinion of J. Bredt and M. Savelsberg[2]), the principal drawback of each of the denominations was that they were too general, *i. e.*, that they comprised too large a number of different classes of chemical bodies under a uniform point of view. Above all, the authors believe that the term "bridge linking" must be defined more preciselly, and for this reason have worked out a new nomenclature for the derivatives of camphane, fenchane, pinane, carane, for compounds of the cyclene type and such with bridged rings with a trimethylene ring attached thereto. In their denomination, they take into consideration, besides the fundamental ring, only the intermediate groups effecting the division of the rings, but take not in account the number of new rings thereby formed. In counting the carbon atoms they start, with regard to the symmetrical structure of the molecule, and if possible, from the carbon atom without a symmetrical counterpart. In contradiction to v. Baeyer, Buchner, and Grignard, the authors differentiate between condensed rings and rings with "bridge linkings". Furthermore, they endeavour to express the structure even of complicated ring-formations, as much as possible, by means of names and not of numbers. In their terminology, all numbers are unmistakeable notations for the position of substituting groups in *cyclo*hexanes with "bridge linkings".

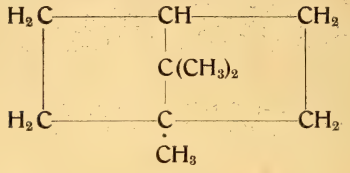
We discuss in the following, *e. g.*, the new nomenclature of the hydrocarbon underlying the derivatives of the camphane and the fenchane series.



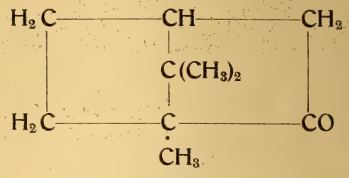
This hydrocarbon possesses two planes of symmetry, one given by the line A—B and the other given by C—D. Where these two planes intersect, there is situated the p-*meso*methylene rest, which in consequence of its special position, being without any symmetrical counterpart, is naturally the startingpoint for counting the carbon atoms. Both the tertiary carbon atoms which occupy the same position with regard to the p-*meso*methylene, are denominated "2", the other four carbon atoms are designed "3". Numbering begins, therefore, with the "bridge" carbon atom, which is termed N° 1, and is continued in either direction up to N° 3. In case a substituting group enters this p-*meso*methylene *cyclo*hexane, there are three possibilities of substitution: either with carbon atom N° 1, with N° 2, or with N° 3. With two or more substitutions, a different position may result, with regard to A—B as well as to C—D. For this reason, a further characterization of the

[1]) Comp. *inter alia* Grignard, *Bull. soc. chim.* IV. **11** (1912), 124; *Report* October **1912**, 143. See also Bredt, *Journ. f. prakt. Chem.* II. **87** (1913), 1; *Report* April **1913**, 146. — [2]) *Journ. f. prakt. Chem.* II. **97** (1918), 1.

numbers 2 and 3 are necessary; 2, 3 and 2 must receive, on the one side of the plane C—D, the additional index α, on the other side the index β. In order to express the further difference with regard to the plane A—B, the atoms 3α and 3β on the one side of A—B receive an additional sign of a hyphen ($3\alpha'$, $3\beta'$), whereas those on the other side remain unaltered. When two substituting groups are attached to the same carbon atom, it is sufficient to repeat the index. Hence, camphane would be termed: p-*meso*methylene-[1,1,2-trimethyl-]*cyclo*hexane, and camphor: p-*meso*methylene-[1,1,2α-trimethyl-]*cyclo*hexan[one-3α].



Camphane.



Camphor.

These examples will probably be sufficient to illustrate the nomenclature worked out by Bredt and Savelsberg; the denominations for other bodies of interest for us, such as fenchane, *iso*fenchane, fenchone, *iso*fenchone, dimethylcamphor, bornylene, camphene, pinene, pinocamphone, tricyclene carboxylic acid, teresantalic acid, &c. may be followed up with aid of the formulæ and explanations of the original paper.

In his paper, "On the condensation of exclusively open-chain-unsaturated systems", H. J. Prins[1]) mentions, *inter alia*, the formation of ionone from *pseudo*ionone.

In connection with his theoretical considerations, he reports on the formation of symm. phenylpropyl glycol from styrene and formaldehyde, with addition of water, where secondarily some polystyrene is formed. Phenylpropyl glycol is a colourless oil, b. p. 145° (12 mm.); boiling with acetic anhydride transforms it quantitatively into the diacetate, b. p. 178° (12 mm). The glycol has a decided smell which must be ascribed to the phenyl radical.

Since the work is mainly theoretical and not fit for a short epitome, we must content ourselves with the above extract.

On allyl compounds. — In their first communication on unsaturated radicals and their chemical and pharmacological behaviour, J. von Braun and Z. Köhler[2]) point out the fact that amongst the aliphatic radicals the unsaturated allyl group takes a position quite for itself. Such manifests itself, *inter alia*, in the loose linking with nitrogen and in some other reactions, for instance in the transformation of the O-allyl phenyl ethers, at elevated temperature, with migration of the allyl group to a carbon atom of the benzene nucleus, a fact which must be explained by the low degree of attachment of the allyl radical to oxygen[3]). The transposition of allyl rhodanide into allyl mustard oil must equally be attributed to the circumstance that the allyl group is in a more loose connection with sulphur as are the saturated alkyls. This transposition passes off far easier as with methyl, ethyl, or other rhodanides. The authors have, furthermore, undertaken some experiments as to the behaviour of the γ-phenyl allyl or cinnamyl radical. They started from cinnamyl alcohol, which was transformed, *viâ* cinnamyl bromide, into cinnamyl dimethylamine. Both of these bodies showed

[1]) *Chem. Weekblad* **14** (1917), 923; *Chem. Zentralbl.* **1918**, I. 168. — [2]) *Berichte* **51** (1918), 79. — [3]) Comp. L. Claisen and O. Eisleb, *Liebig's Ann.* **401** (1913), 21; *Report* April **1914**, 144.

to be exactly analogons to the corresponding allyl derivatives; the bromide was easily hydrolyzed by water and easily added to tertiary bases, &c. Cinnamyl bromide showed the m. p. 31 to 32°. It may be assumed that cinnamyl chloride would readily pass over into cinnamyl mustard oil, as well as cinnamyl phenyl ether suffer Claisen's rearrangement, both questions which the authors, at present, were unable to decide.

Hydrocarbons.

A new method for preparing some unsaturated hydrocarbons. — B. T. Brooks and J. Humphrey[1]) examined the reactions passing off in the refining of petroleum distillates, such as are usually carried out in the petroleum refineries. It was principally the question of the action of concentrated sulphuric acid on unsaturated aliphatic hydrocarbons, yet the authors describe, in addition, some reactions which are of interest with regard to our special branch. For the preparation of hydrocarbons from secondary or tertiary alcohols they recommend distillation with iodine, this method giving better yields than the other ones commonly used. Menthol, for instance, splits off water easily on slow distillation with addition of 1 per cent. iodine; a hydrocarbon is formed thereby (b. p. 169 to 170°, $d\frac{20°}{4°}$ 0.811) which is probably identical with Wallach's[2]) menthene of the same boiling point. When 119 cc. of this hydrocarbon are shaken with 100 cc. sulphuric acid of 85 per cent. strength dimenthene $C_{20}H_{36}$ (b. p. 310 to 315°; d 0.899; n_{D200} 1.4795) is formed with a yield of 55 per cent. The sulphuric acid contained an oil smelling of menthol, but no crystalline body could be prepared therefrom.

Furthermore, they studied the action of sulphuric acid on α- and β-pinene, limonene, and myrcene. When sulphuric acid of 85 per cent. is added, at 0°, to α-pinene, the principal product is a dimeric substance $C_{20}H_{32}$, b. p. 170 to 175° (15 mm.), in addition to a viscid trimeric body. When fractionating the first runnings a smell of borneol was noticed, but it was not possible to isolate a crystalline compound. On acting with a sulphuric acid of 72 per cent., at 25°, the dimeric hydrocarbon resulted in a yield of 62 per cent. β-Pinene, as well as limonene, behaved in the same manner.

In order to obtain myrcene, the authors heated 270 g. linalool for two hours with 3 g. iodine, when nearly the theoretical amount of water was split off. On fractionating the reaction-mixture, they obtained 103 g. myrcene (b. p. 165 to 167°), 24 g. of a fraction b. p. 167 to 177°, evidently a mixture of myrcene and limonene, as well as about 143 g. unattacked linalool and polymerization products. Myrcene reacted so violently with sulphuric acid of 85 per cent. that resinification, carbonisation, and oxidation could not be prevented.

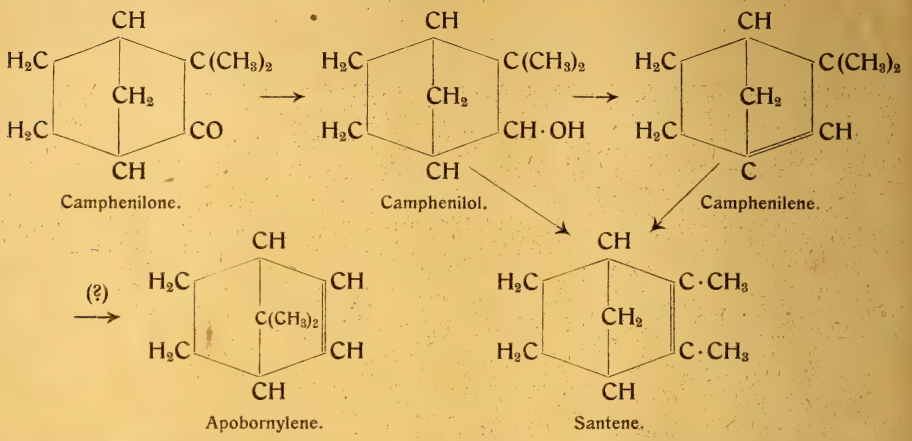
Styrene, when treated with sulphuric acid of 85 per cent., gave rise solely to the resinous polymeride, phenylethyl alcohol not being formed.

Camphenilene. — Some years ago, S. V. Hintikka and G. Komppa[3]) described the transposition of camphenilone into *iso*camphenilone. Camphenilone was reduced to camphenilol, this alcohol transformed into camphenilyl chloride and the latter, by abstraction of hydrogen chloride, into camphenilene; from this hydrocarbon, by the usual method, *iso*camphenilyl acetate, and by oxidizing the free alcohol, *iso*camphenilone was obtained.

[1]) *Journ. Amer. chem. Soc.* **40** (1918), 822. — [2]) *Liebig's Ann.* **300** (1898), 282. — [3]) *Liebig's Ann.* **387** (1912), 293; *Report* April **1912**, 187.

As early as in 1914 H. Meerwein[1]) had pointed out that the exclusive formation of camphenilene, on abstracting water from camphenilol, would be remarkable and he suspected that it here might be the case of santene. His expectation has now turned out to be correct, since Komppa and Hintikka[2]) have found that the camphenilene prepared from camphenilone is no uniform substance, but a mixture of at least two different hydrocarbons.

When accepting Semmler's formula for santene and terming the normal product of the reaction *camphenilene*, the following series of reactions is obtained: —



The santene has been formed from camphenilol or camphenilene by a pinacolin rearrangement thus putting the santene formula of Semmler on a sound basis.

The *iso*camphenilol described by Komppa and Hintikka in their previous work is, therefore, identical with santenol (= π-norborneol of Semmler), *iso*camphenilone identical with santenone (= Semmler's π-norcamphor).

For preparing camphenilene, the authors heated a mixture of camphenilol with sodium hydrogen sulphate for one hour in an oil bath up to 190 to 200°. The hydrocarbon was removed from the reaction product by careful distillation, then washed with soda solution and, after drying with anhydrous sodium sulphate, fractionated. Besides small fractions of b. p. 136 to 138° and 138 to 141° a principal fraction of b. p. 140 to 142° was obtained. The constants of the latter ($d_{4^\circ}^{17^\circ}$ 0.8700; n_{D17° 1.46758) were in full accord with those of santene (d_{15° 0.8698; $n_{D17.5^\circ}$ 1.4688). The product obtained from camphenilyl chloride by action of aniline gave on fractional distillation a part b. p. 136 to 140° and one of the b. p. 140 to 142°. The nitrosite of this higher-boiling portion showed the m. p. 122 to 124° and gave, after mixing with the nitrosite of santene, no depression in the melting point.

In order to identify the hydrocarbon obtained from camphenilol by dehydration Komppa and Hintikka prepared the acetate by Bertram and Walbaum's method; b. p. 212 to 214°; $d_{4^\circ}^{20^\circ}$ 0.9875; n_{D20° 1.45983. The acetate prepared from santene according to Aschan showed: $d_{4^\circ}^{20^\circ}$ 0.9871; n_{D19° 1.45929. On saponification, there results from the acetate an alrohol, m. p. 60 to 65°, b. p. 193 to 195°, from which by oxidation a ketone was obtained, the semicarbazone of which showed the m. p. 225 to 226° and after mixing with santenone semicarbazone gave no depression in the melting point. The ketone obtained previously and designated as *iso*camphenilone yielded a

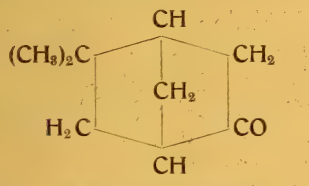
[1]) *Liebig's Ann.* **405** (1914), 134. — [2]) *Bull. soc. chim.* IV. **21** (1917), 13.

semicarbazone which on mixing with santenone semicarbazone likewise gave no melting point depression. From the alcohol "*iso*camphenilol" derived from this "*iso*-camphenilone" there was prepared, by oxidation with potassium permanganate, an acid, m. p. 170 to 171°, which constant was not altered after mixing with santenil acid.

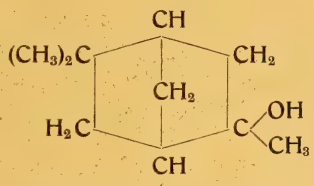
It is clear from the results of this investigation that doubtless the hydrocarbon originating from camphenilyl chloride or from camphenilol contains santene; probably it is contaminated with apobornylene.

Fenchene. — G. Komppa and R. H. Roschier[1]), some years ago, performed the synthesis of α-fenchene by starting from rac. α-fenchocamphorone. Recently[2]), they investigated the products formed from rac. β-fenchocamphorone by analogous treatment. When it is acted upon by methylmagnesium iodide, the latter ketone gives rise to methyl-β-fenchocamphorol (II) m.p. 66 to 67°; b.p. 77° at 9 mm.), the phenylurethane of which melts at 133.5 to 134°. On heating with potassium hydrogen sulphate, a mixture of hydrocarbons results from methyl β-fenchocamphorol, which consists in the main of rac. β-fenchene (III) (b.p. 151 to 153°; $d_{20°}$ 0.8596; $n_{D20°}$ 1.46581) and an endocyclic fenchene termed γ-fenchene (IV) (b.p. 146 to 148°; $d^{20°}_{4°}$ 0.8539; $n_{D20°}$ 1.46063). The latter is identical with the hydrocarbon obtained from rac. fenchylalcohol and potassium hydrogen sulphate.

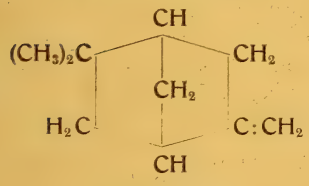
The endocyclic fenchene discovered by Roschier[3]) in a different connection shall now be termed δ-fenchene or *iso*fenchene. The hydrocarbon (III) designated by the authors as β-fenchene was named by Semmler *iso*fenchene, by Wallach *D,d*- or *L,l*-fenchene. What now is termed δ- or *iso*fenchene had been named iso*allo*fenchene by Semmler and *iso*fenchylene by Qvist[4]).



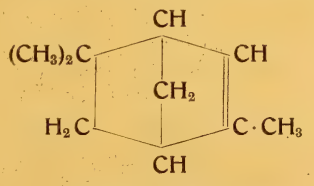
(I) β-Fenchocamphorone.



(II) Methyl β-fenchocamphorol.



(III) β-Fenchene.



(IV) γ-Fenchene.

Cymene. — We wish to draw the attention of our readers to a publication of A. W. Schorger[5]) on the action of aluminium chloride on cymene. So-called sulphite turpentine oil was freed from an impurity, possibly a terpene, by shaking with sulphuric acid; the purified cymene had the constants: b.p. 176 to 176.6°; $d_{20°}$ 0.8575; $n_{D20°}$ 1.4908; thioamide, m.p. 114°. On oxidation, *p*-hydroxy*iso*propylbenzoic acid was

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[1]) *Ann. Acad. Scient. Fennicæ, Ser.* A, *vol.* X. **3** (1916), 3; *Chem. Zentralbl.* **1917**, I. 751; *Report* October **1917**, 144. — [2]) *Ann. Acad. Scient. Fennicæ, Ser.* A, *vol.* X. **15** (1917), 622; *Chem. Zentralbl.* **1918**, I. 622. — [3]) *Ann. Acad. Scient. Fennicæ, Ser.* A, *vol.* X. **15** (1917), 1; *Chem. Zentralbl.* **1918**, I. 622. — [4]) Comp. *Report* November **1908**, 190. — [5]) *Journ. Amer. chem. Soc.* **39** (1917), 2671.

formed. The action of aluminium chloride was carried out at different temperatures, when the formation of the following hydrocarbons was observed: di*iso*propyl, benzene, toluene, *m*-xylene, and *1*-methyl-*3,5*-di*iso*propylbenzene, a body unknown hitherto. Schorger characterized all of these hydrocarbons by suitable derivatives.

Alcohols.

Cyclo*hexyl-4-butanol-3*. — When *cyclo*hexanol, *sec.* butylalcohol and dehydrated potassium hydroxide are heated for 24 hrs. in a sealed tube to 210 to 220°, there results, as has been found by M. Guerbet[1]), the secondary alcohol *cyclo*hexyl-*4*-butanol-*3*, a colourless liquid of weak but pleasant smell; b.p. 126 to 127° (31 mm.), $d_{19°}$ 0.932; acetate, b.p. 131 to 132° (31 mm.); phenylurethane, m.p. 76°. Oxidation of the alcohol by means of potassian bichromate and sulphuric acid led to the corresponding ketone *cyclo*butyl-*4*-butanone-*3*, a pleasant-smelling liquid; b.p. 220 to 222 (758 mm.), $d_{0°}$ 0.917. The ketone does not react with sodium hydrogen sulphite. Its semicarbazone melts at 145 to 146°. Further oxidation of the ketone by means of potassium bichromate and sulphuric acid yielded a mixture of acetic and *cyclo*hexylacetic acids.

$$\underset{\text{Cyclohexanol.}}{C_6H_{11}\cdot OH} + \underset{\text{sec. Butylalcohol.}}{CH_3\cdot CHOH\cdot CH_2\cdot CH_3} = \underset{\text{Cyclohexyl-4-butanol-3.}}{C_6H_{11}\cdot CH_2\cdot CHOH\cdot CH_2\cdot CH_3} + H_2O$$

Menthol.—The menthyl chloride originating from the action of phosphorus pentachloride or concentrated hydrochloric acid on menthol is no uniform substance, but a mixture of at least two isomerides. Pure methyl chloride proper was prepared at one time by M. J. Kursanov[2]) by boiling the crude product with alcoholic potash or aniline. Recently, the same author[3]), in order to study the composition of raw menthyl chloride, has investigated the different menthane carboxylic acids resulting therefrom. The stable menthyl chloride yields only one menthane carboxylic acid, m.p. 65 to 66°, the raw product yielding also a liquid acid. No stereoisomeric transformation takes place where phosphorus trichloride acts on the solid acid, since the chloro-anhydride obtained can be retransformed into the original acid. The acid of the m.p. 65 to 66° ($[\alpha]_D$ — 54.23° in benzene solution) yields a crystalline amide, m.p. 151°; the liquid acid is possibly a mixture of several isomeric acids.

In order to investigate the composition of "menthyl chloride", Kursanov[4]) studied the behaviour of two different preparations obtained by the action of phosphorus pentachloride on a solution of menthol in light petroleum. The one boiled from 90 to 95° (16 mm.) (α_D — 10.68° [in a 20 cm. tube]), the other from 91 to 96° (16 mm.) (α_D — 14.50° [in a 20 cm. tube]). Both preparations were repeatedly heated with alcoholic potash, and each time the volatile portion removed and undecomposed chloride again heated with alcoholic potash. It was found that the optical rotation of the first fractions increased at first, then decreased; in the ead, the positive rotation changed into the negative.

Since the stable menthyl chloride, even after mixing it with menthyl chloride prepared from menthene and hydrogen chloride, remains unattacked when boiling with alcoholic potash, Kursanov assumes that the crude preparation is composed of a mixture of the stable menthyl chloride, two secondary chlorides of different rotatory

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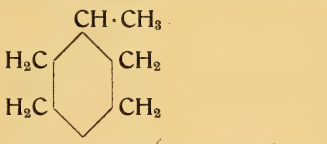
[1]) *Bull. Soc. chim.* IV. **23** (1918), 78. — [2]) Comp. *Report* October **1901**, 72. — [3]) *Journ. Russ. phys.-chem. Soc.* **48** (1916), 862; *Journ. chem. Soc.* **112** (1917), I. 137. — [4]) *Journ. Russ. phys.-chem. Soc.* **48** (1917), 367; *Journ. chem. Soc.* **112** (1917), I. 151.

power, and an optically inactive tertiary chloride. Both his crude preparations were believed to contain about 47.31 and 44.44 p.c. stable menthyl chloride.

Kursanov[1]) then describes the preparation of a dextrorotatory menthyl iodide. Menthyl acetate (α_D — 73.05°) was saturated in chloroform solution, at — 20°, with dry hydrogen iodide and the mixture let to stand in a sealed glass tube for five days. The resulting menthyl iodide boiled at 122 to 123° (17 mm.). Three different preparations showed α_D + 41.2, + 35.13 and + 37.62°. When this menthyl iodide is boiled with alcoholic potash the same menthene results as from the lævorotatory menthyl haloids. On heating with sodium in ethereal solution the same mixture of dimenthyl, menthane, and menthene is obtained from the dextrorotatory menthyl iodide as from the ordinary menthyl haloids.

Menthyl iodide may also he prepared from menthyl hydrogen phthalate; b.p. 121 to 122° (17 mm.), α_D — 13.44°. Menthyl bromide, prepared by Kursanov in various manners, showed α_D — 5.20 and — 23.35°.

In continuation of earlier publications[2]) Kursanov[3]) reports on the various menthylphenols. He found that from the mixture of different menthyl phenols resulting from phenyl menthylether by boiling with hydrochloric acid, phenylurethanes of different melting points are formed. Crystalline menthyl phenol, when heated in a sealed glass tube with hydrochloric acid, is partially decomposed into optically inactive menthyl chloride, whereas the undecomposed part is isomerised to a mixture of crystalline and liquid menthyl phenols. The author attributes to menthyl phenol the following formula:—



Menthylphenol.

He believes to have proved the tertiary nature of menthyl phenol by chemical means.

H. Wren and C. J. Still[4]) have published a paper on the *l*-menthyl ester of the diphenyl succinic acids, where they describe the action of menthol on *l*- and on *d*-diphenylsuccinic acid and derivatives of these acids. For the experimental details of the publication we beg to refer to the original paper.

Concerning the different crystallization forms of menthol and their mutual transformation, *vide* p. 96 of this *Report*.

Pinol hydrate. — On p. 165 of our *Report* April **1911** we reported on the reduction of *i*-pinol hydrate performed by Wallach, where a body of the formula $C_{10}H_{20}O_2$ resulted, the composition of which was not elucidated, but which was believed to be identical with *2,8*-menthanediol resulting from dihydrocarveol by addition of water. This acception has proved to be erroneous, as Wallach[5]) states in his 120th paper On Terpenes and Essential Oils; he had found formerly that the *i*-glycol from dihydrocarveol melted at 108 to 109°, whereas the glycol (dihydropinol hydrate) resulting from *i*-pinol hydrate melts at 139 to 141°.

Wallach now extended his investigations on dextrorotatory pinol hydrate (sobrerol) furnished by us ($[\alpha]_D$ + 141° 16′ [7.05 p.c. alcoholic solution]; m.p. 148 to 149°). The reduction of this sobrerol was performed in alcoholic solution according to Paal's

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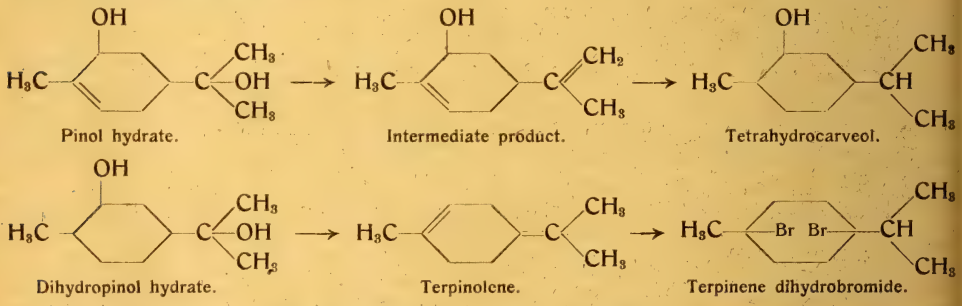
[1]) *Journ. Russ. phys.-chem. Soc.* **48** (1916), 1151; *Journ. chem. Soc.* **112** (1917), I. 396. — [2]) Comp. *Report* October **1915**, 79. — [3]) *Journ. Russ. phys.-chem. Soc.* **48** (1916), 1156; *Journ. chem. Soc.* **112** (1917), I. 396. — [4]) *Journ. chem. Soc.* **111** (1917), 513. — [5]) *Liebig's Annalen* **414** (1917), 195.

method and led to a glycol $C_{10}H_{18}(OH)_2$, m.p. 158 to 159°; $[\alpha]_D$ — 40° 26′, whereas the saturated glycol prepared formerly by hydration of active dihydrocarveol melted at 113 to 114°. Evidently there are marked differences in the properties of these preparations taken first for identical bodies, in those of the active as well of the inactive preparations.

In order to elucidate these relations Wallach undertook some more experiments. He found that on treating pinol hydrate with free hydrogen in presence of colloidal palladium and of free acid a secondary reaction took place, in addition to the principal one, which had also been observed formerly[1]), *i. e.*, that colloidal palladium abstracts easily water from unsaturated glycols, even at ordinary temperature. Primarily, an unsaturated monovalent alcohol results which passes over into the saturated monovalent alcohol by reduction.

When reducing the odourless *i*-pinol an alcohol could be easily isolated from the reaction by steam-distillation, which proved to be tetrahydrocarveol. Hereby it was demonstrated anew that not always unsaturated glycols may be reduced evenly into saturated glycols in presence of a colloidal metal. At any rate, the formation of tetrahydrocarveol is a new proof for the fact that in pinol hydrate one hydroxyl is linked in position 2. Another fact observed by Wallach in the behaviour of pinol hydrate was apt to raise doubts as to the correct position in pinol hydrate of both the hydroxyl groups. When, namely, *i*-dihydropinol hydrate, m.p. 139°, was treated with acetic acid saturated with hydrobromic acid, there is formed, either at once or after some standing, terpinene dihydrobromide, m.p. 58°. The same dihydrobromide results from active dihydropinol hydrate. The course of both reactions is illustrated by the following formulæ: —



Menthane-diol-2,8 from dihydrocarveol does not show this reaction, neither was it observed when dihydropinol hydrate was treated with acetic acid + hydrochloric acid in lieu of acetic acid + hydrobromic acid. This negative result may, however, he explained by the formation of a mixture of dihydrochlorides which generally show a very low melting point.

Wallach found furthermore that from the last mother-liquors from the crystallization of the product resulting from the reduction of *i*-pinol hydrate, there is obtained, in addition to dihydropinol hydrate of the m.p. 139 to 140°, a body with the structure of dihydropinol hydrate which solidified only slowly and was difficult to purify; it melted at 104 to 106°; evidently it was not identical with the menthanediol obtainable from dihydrocarveol. Since menthane-2,8-diol contains several asymmetric carbon atoms and hence must be able to exist in several stereoisomeric forms, Wallach has

[1]) *Liebig's Annalen* **392** (1912), 60; *Report* October **1912**, 114.

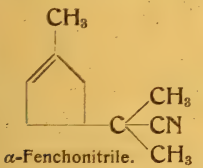
tried to obtain different glycols by starting from carvone and by altering the conditions of their formation. However, this could not be realized, probably for the reason that carvone itself contains only one asymmetric carbon atom.

On comparing dihydropinol hydrate with other glycols of isomeric structure the following facts were found: Menthane-*1,4*-diol, m.p. 137 to 138°, obtainable by various methods, is entirely different from *i*-dihydropinol hydrate. A second menthane-*1,4*-diol had been obtained from ascaridol[1]). Dihydropinol hydrate was furthermore compared with the menthane-*2,4*-diol obtainable from sabinene glycol. On treating sabinol with diluted sulphuric acid there results a glycol the structure of which, it is true, is not yet quite elucidated[2]), and which on reduction according to Paal yields a glycol probably identical with menthane-*2,4*-diol. It could not be recrystallized, melts, after pressing, at 93 to 94°, and is certainly not identical with dihydropinol hydrate.

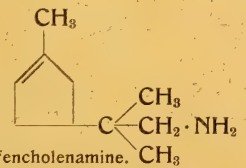
With the object of studying the behaviour of the unsaturated glycol from sabinene glycol, Wallach treated it with oxalic acid in order to abstract water therefrom. A mixture was obtained containing a hydrocarbon giving the reaction for terpinene, and an unsaturated alcohol which by its constants and its derivatives proved to be carvenol, Δ^3-menthenol-*2*, since by oxidation carvenone, by reduction tetrahydrocarveol were obtained. In this alcohol there may be contained $\Delta^{4(8)}$-menthenol-*2*, which may be formed from menthane-*2,4*-diol by dehydration equally well as carvenol.

On decomposing *i*-dihydropinol hydrate with oxalic acid a mixture resulted, the principal constituent of which was an oxide of cineole-like smell, besides dihydrocarveol. Rupe[3]) has proved years ago that menthane-*2,8*-diol could be split up in the same manner by aid of acids.

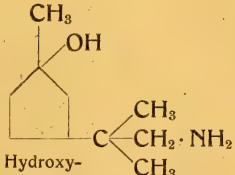
Dihydrofencholene alcohol. — Many years ago, Wallach[4]) described the reduction, with sodium and alcohol, of α-fenchonitrile, when fencholenamine results, and additionally hydroxyfencholenamine, on using anhydrous alcohol. When fencholenamine is brought to react with nitrous acid, there results not the unsaturated alcohol, as was to be expected, but, with molecular rearrangement, a tertiary alcohol. This alcohol wes reduced by Wallach[5]) to the saturated body dihydrofencholene alcohol by aid of Paal's method and adding acetone. It had a pleasant smell. On reducing α-fenchonitrile with sodium there was obtained, in addition to fencholenamine, its hydrate, a viscid liquid, b. p. 134° (15 mm.) which could not be brought to solidify. On treatment with sodium nitrite and glacial acetic acid, the hydroxy base yielded fencholenalcohol and a glycol $C_{10}H_{18}(OH)_2$, m. p. 103 to 104°.



α-Fenchonitrile.



Fencholenamine.



Hydroxy-fencholenamine.

Iso*amylcarvenol.* — On p. 21 of our *Report* **1917** we described *inter alia* the sesquiterpene alcohol *iso*amyldihydrocarveol abtained by Semmler and Oelsner as by-product of *iso*amyldihydrocarvone. As we gather from a new paper of F. W. Semmler,

[1]) *Liebig's Annalen* **392** (1912), 61; *Report* October **1912**, 114. — [2]) *Liebig's Annalen* **360** (1908), 100; *Report* April **1908**, 166. — [3]) *Berichte* **38** (1905), 1723. — [4]) *Liebig's Annalen* **263** (1891), 138; **269** (1891), 369. — [5]) *Ibidem*, **414** (1917), 227.

K. G. Jonas and K. Oelsner[1]), it is here not the question of *iso*amyl*dihydro*carveol, $C_{15}H_{28}O$ but of *iso*amylcarveol $C_{15}H_{26}O$. By treatment with potassium hydrogen sulphate the alcohol split off water with formation of *iso*amyl-dehydrophellandrene. Reduction of the tertiary *iso*amylcarveol with platinum and hydrogen in absolute-ethereal solution led to the saturated alcohol $C_{15}H_{30}O$, tertiary *iso*amyltetrahydrocarveol. The secondary *iso*amyldihydrocarveol obtained by reduction of *iso*amyldihydrocarvone (oxime m. p. 135°) yielded by reduction with the same means secondary *iso*amyltetrahydrocarveol.

*Iso*amyldihydrocarveol is obtained from *iso*amyldihydrocarvone by reduction with sodium and alcohol. B. p. 150 to 155° (10 mm.); $d_{20°}$ 0.8993; $\alpha_D + 1°$; $n_{D20°}$ 1.47449. Its acetate boiled from 155 to 160° (11 mm.); $d_{20°}$ 0.9227.

A research on *betulol* has been dealt with on p. 9 of this *Report*.

Aldehydes.

In a communication on *a new method for the preparation of aldehydes* K. W. Rosenmund[2]) draws attention to the fact, that, whereas the carboxylic acids, in general, are easily accessible, the formation of the aldehydes is far more difficult, bodies which are far more reactive and hence of scientific and commercial importance. Many attempts have been made to transform acids into aldehydes, but hardly any reactions of general applicability have been found out. The most successful method, the distillation of carboxylates with formiates, is restricted to those aldehydes which are distillable without decomposition. Experiments to get at the aldehydes direct from the acid halides by reduction with hydrogen have hitherto not been successful. As Rosenmund, however, has found, the reduction of acid chlorides by means of hydrogen in presence of a catalyst can be successfully performed, it depends only upon correct disposition of the conditions upon which the reaction is carried out. Just those conditions which were chosen from the theoretical point of view proved to be unsuitable. The following, namely, seemed to be of importance: 1. low temperature, in order to obviate further reduction of the aldehyde formed; 2. working in closed apparatus, so as to measure the hydrogen consumed; 3. working without a solvent or in such a solvent which would not poison the catalyst or react with the acid chloride, as which solely ether would come into consideration; 4. removal of the hydrogen chloride formed.

Now, exactly those conditions led to good results which differed strongly from the above principles: working in open apparatus, use of benzene hydrocarbons as solvent, application of high temperature and disuse of absorbents for hydrogen chloride. Since the latter is nearly insoluble in benzene hydrocarbons it escapes immediately after its formation and does no harm to the catalyst. As such Rosenmund employed palladium precipitated on barium sulphate (content 5 per cent. Pd); nickel proved also to be effective.

For the preparation of benzaldehyde from benzoyl chloride, Rosenmund proceeds as follows: 5 g. benzoyl chloride are dissolved in 25 cc. dry xylene, 2 g. of the catalyst added and hydrogen is passed through the boiling mixture so long until the evolution of hydrogen chloride has come to an end. On shaking the xylene solution with concentrated bisulphite solution the double salt of bisulphite-benzaldehyde separates off in nearly theoretical yield. Without a solvent the yield decreases very strongly, also when other solvents are used. For instance, the yield with xylene was 71 per cent., with ether 2.1 per cent. By the same method Rosenmund prepared butylaldehyde from

[1]) *Berichte* **50** (1917), 1838. — [2]) *Berichte* **51** (1918), 585.

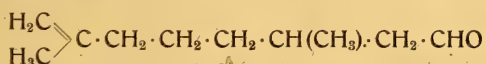
butyryl chloride; yield in ethereal solution, 50 p. c. Stearyl chloride in xylene gave also a good yield of stearaldehyde in xylene solution.

Benzoylated cyanohydrines of various aldehydes. — J. Aloy and C. Rabaut[1]) have prepared the benzoylated cyanohydrines ann the corresponding amides and acids of several aldehydes which are of interest for our special industry. In order to prepare these derivatives, an equimolecular mixture of potassium cyanide and of the aldehyde in water is treated with benzoyl chloride and the reaction-product extracted with ether. Cinnamic aldehyde forms a benzoylcyanohydrine m. p. 66 to 67°, the derivative of cuminaldehyde melts at 65°. The benzoylcyanohydrine of cinnamic aldehyde, on treatment with acetic acid and zinc, or cupric oxide, passes over into the corresponding amide. The amide corresponding with the benzoylated cyanohydrine of cuminaldehyde has the m. p. 182°, that of œnanthaldehyde: 104 to 105°. The benzoyl cyanohydrines of valeric and œnanthic aldehydes, of citral, menthone, and pulegone were obtained only as syrupy masses.

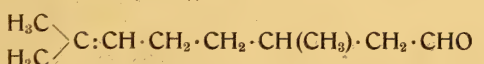
Citronellal. — From the investigations of C. Harries and A. Himmelmann[2]) it must be accepted that citronellal is no uniform body, but a mixture of two isomeric aldehydes citronellal (I) and rhodinal (II). Later investigations of Harries and F. Comberg[3]) have confirmed this view, but it was hitherto impossible to isolate the two isomerides. Now, H. J. Prins[4]) has endeavoured to effect this separation. From Java citronella oil he obtained by fractionation two parts, the one of the b. p. 200° (semicarbazone, m. p. 78°; semioxamazone, m. p. 183 to 184°) and the other of the b. p. 198° (semicarbazone, m. p. 81 to 82°; semioxamazone, m. p. 185.5 to 186.5°). Citronellal thus prepared was purified by means of the bisulphite compound according to Tiemann and Schmidt[5]) and yielded the following fractions:—

Citronellal I	Citronellal II
B. p. 203 to 204°	B. p. 198 to 199°
$n_{D18°}$ 1.45882	$n_{D16°}$ 1.45742
M. p. of semicarbazone 85.5 to 86°	M. p. of semicarbazone 83 to 84°
„ „ semioxamazone, 184 to 186°	„ „ semioxamazone 189 to 190°

Attenpts to separate the two bisulphite compounds on account of their different solubility in alcohol were without success.



(I) Citronellal.



(II) Rhodinal.

Furthermore, Prins transformed a considerable amount of citronellal, 700 g., into the bisulphite compound, washed the latter with much benzene, then with some litres of alcohol, dried sharply at the suction pump and decomposed the compound with potash solution in presence of much ether, chilling during this operation. After washing with very diluted acetic acid he distilled the oil separated *in vacuo* (15 mm.), the whole

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[1]) *Bull. Soc. chim.* IV. **23** (1918), 98. — [2]) *Berichte* **41** (1908), 2187; *Report* October **1908**. 185. — [3]) *Liebig's Annalen* **410**, (1915), 1; *Report* October **1915**, 73. — [4]) *Chem. Weekblad* **14** (1917), 692. — [5]) *Berichte* **29** (1896), 904; *Report* October **1896**, 90.

passing over between 90 and 110°. After repeated fractionation the following fractions of constant boiling points were obtained: —

Citronellal I	Citronellal II
B. p. 203 to 204°	B. p. 198 to 200°
$d_{14°}$ 0.8880	$d_{14°}$ 0.8745
$n_{D14°}$ 1.46141	$n_{D14°}$ 1.45482
M_d 47.68	M_d 47.09
Semicarbazone, m. p. 85 to 86°	Semicarbazone, m. p. 82.5 to 83°

M_d calculated 47.92.

Both citronellals yield quantitatively a semicarbazone which is easily soluble in chloroform, but nearly insoluble in cold low-boiling light petroleum. The semicarbazone of citronellal I is oily and crystallizes at ordinary temperature only partly, that of citronellal II, however, crystallizes at once. The melting points are difficult to obtain constant, because both semicarbazones are slightly optically active and therefore form a mixture of the active and the racemic semicarbazones. By repeated recrystallization the racemic product is obtained in the end.

The semioxamazones are formed on heating the both ingredients in 50 per cent. alcohol on the water bath. The reaction passes off very rapidly; on chilling the body separates off in form of an indistinct crystalline mass which may be freed from an excess of semioxamazide by boiling with water. These semioxamazones dissolve, *inter alia,* in toluene and amylalcohol as colloids and form gels on cooling; from alcohol they crystallize well on slow cooling.

Starting from the constants observed Prins accepts for citronellal I the formula I (*ω*-citronellal, or citronellal *sensu strictiori*), for citronellal II the formula II (symmetrical citronellal, or rhodinal).

Whe are of opinion that Prins had not to deal with pure citronellals; specific gravity and refraction being far too high make it most probable that he had to do with products either strongly contaminated with *iso*pulegol or highly resinified. The constants found by Prins differ greatly from all data given by various investigators[1]) for density and refraction of citronellal and range for beyond the values even of commercial preparations which fluctuate for $d_{15°}$ between 0.855 and 0.860, for $n_{D20°}$ from 1.444 to 1.449. Whe think it a failure to draw conclusions as to the structure of such impure preparations.

As Prins[2]) has observed, the transition of citronellal into *iso*pulegol is easily effected by treatment of this aldehyde with formic acid of 85 to 90 per cent. or of phosphoric acid of 80 per cent. He mixed citronellal with the five-fold amount of formic acid, chilling constantly with ice, and let the mixture stand for a night in ice, poured it then in water and washed the reaction-product with diluted sodium carbonate solution. The oil obtained hereby was saponified with a little more than the theoretical amount of alcoholic potash. By fractionated distillation be obtained from the saponified oil about 10 per cent. *iso*pulegol, 10 to 20 per cent. residue (consisting of a condensation-product from two molecules of citronellal), and 75 to 80 per cent. of a fraction of the b. p. 140 to 160° (13 mm.). This fraction, after repeated fractionation, boiled constant at 145° and, after dissolving in low-boiling light petroleum, separated off on cooling down to — 20° in form of crystals melting at 84 to 85°. The mother-liquor contained a body of the m. p. 60 to 62°. The compound of m. p. 84 to 85° is, in Prins' opinion, identical with Wallach's *iso*pulegol hydrate obtained by shaking *iso*-

[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed. vol. I. p. 415. — [2]) *Chem. Weekblad* **14** (1917), 627.

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pulegol with diluted sulphuric acid, or Ph. Barbier's and G. Léser's[1]) menthoglycol. Wallach[2]) states for *iso*pulegol hydrate the m. p. 75°[4]), Barbier and Léser for their menthoglycol the m. p. 81 to 81.5°. Perhaps the body contained in the mother-liquor is an isomeride of menthoglycol.

Asarylaldehyde. — Some years ago, R. Fabinyi and T. Széki[3]) pointed ont the fact that asarylaldehyde (*2,4,5*-trimethoxybenzaldehyde), under ordinary circumstances, does not show normal reaction with organomagnesium halides. In this reaction, there are formed not the secondary alcohols, as might be expected, but ether-like combinations resulting from two molecules of the carbinols by dehydration. This abnormal course of the reaction is in all probability to be ascribed to the special position of the methoxyl groups in the asaryl molecule. For this reason the authors[5]) expected to arrive at analogous ether-like compounds when starting from apiolaldehyde, a body closely related to asarylaldehyde. Here the reaction proceeded in dependance on the *modus procedendi, i. e.,* the ether-like bodies being formed not always, but also the normal secondary alcohols. For instance, the interaction of magnesium methyl iodide with apiolaldehyde led to dimethoxy methylenedioxy phenyl methyl carbinol $(CH_3O)_2:(CH_2O_2):C_6H\cdot CH(OH)\cdot CH_3$, m. p. 52°. In this reaction, the solution of magnesium methyl iodide in ether was gradually treated, with strong cooling, with a suspension of apiolaldehyde in benzene. When, however, a luke-warm solution of apiolaldehyde in benzene is given to the solution of magnesium methyl iodide in ether, symm. di-(dimethoxy methylenedioxy phenyl) ethyl ether $[(CH_3O)_2:(CH_2O_2):C_6H\cdot CH(CH_3)]_2O$ is formed, a white crystalline product of the m. p. 122°.

When apiolaldehyde, suspended in benzene, is allowed, with strong cooling, to act on the theoretical amount of magnesium ethyl iodide, the result is the normal secondary alcohol, dimethoxy methylenedioxy phenylethyl carbinol $(CH_3O)_2:(CH_2O_2):C_6H\cdot CH(OH)\cdot C_2H_5$ m. p. 54°. But on treating apiolaldehyde with magnesium ethyl iodide without cooling, the ether-like compound, symm. di-(dimethoxy methylenedioxy phenyl) propyl ether, m. p. 112°, is formed.

From, phenyl magnesium iodide and apiolaldehyde, the normal carbinol, phenyl dimethoxy methylenedioxy phenyl carbinol $(CH_3O)_2:(CH_2O_2):C_6H\cdot CH(OH)\cdot C_6H_5$, white crystals, m. p. 72°, is obtained.

For the preparation of apiolaldehyde, Fabinyi and Széki oxidize *iso*apiol not in the usual manner with chromic acid or with potassium bichromate, but with ethyl nitrite; the reaction proceeds evenly and the yield is considerably higher than when working according to the old method. For this purpose the authors mix a solution of 10 g. *iso*apiol in 50 ccm. ethyl alcohol in a flask mounted by a reflux condenser, through the latter with 7 ccm. freshly prepared ethyl nitrite and add quickly 4.5 ccm. concentrated hydrochloric acid. Oxidation proceeds at once without application of heat, the liquid begins to boil so that it is necessary to mitigate the course of the reaction by immersing the flask in cold water. In a short time after termination of the reaction (during in the utmost 10 minutes) the contents of the flask solidify into a thick mass of crystals. The yield of apiolaldehyde is on the average 40 to 45 per cent. By the same manner, asarone could be oxidized to asarylaldehyde, equally with very good yield.

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[1]) *Compt. rend.* **124** (1897), 1308. — [2]) *Liebig's Annalen* **360** (1908), 103. — [3]) Not 72°, as quoted by Prins. Besides, Wallach only regards it as *probable* that his *iso*pulegol hydrate might be identical with Barbier's and Léser's menthoglycol; Prins, however, regards them actually as identical. — [4]) *Berichte* **39** (1906), 1218. — [5]) *Ibidem* **50** (1917), 1335.

Ketones.

On p. 127 of our *Report* **1916** we dealt with a paper published by Wallach "On a method for transformation of hexacyclic ketones into *cyclo*pentanones" in a short communication in the *Nachrichten der K. Gesellschaft der Wissenschaften,* Göttingen. The experimental details of this work have in the meantime been published by Wallach[1]) elsewhere, so that now we are in the position to supplement our former abstract. The primary raw material for his investigations were two easily accessible ketones, *i. e.,* menthone and tetrahydrocarvone (carvomenthone), from which various dibromo derivatives may be prepared readily. Hereby the following dibromomenthones are obtainable: — 1. *4,8*-Dibromomenthone, by addition of bromine to pulegone; 2. *1,2*-dibromomenthone, by addition of bromine to Δ^1-menthenone-*3*; 3. *4,5*-dibromomenthone by addition of bromine to Δ^4-menthenone-*3*; 4. *2,4*-dibromomenthone by direct bromination of menthone. — In the carvomenthone series, there is formed: — *3,4*-dibromocarvomenthone by addition of bromine to carvenone; *8,9*-dibromocarvomenthone by addition of bromine to dihydrocarvone; *1,6*-dibromocarvomenthone by addition of bromine to carvotanacetone; *1,3*-dibromocarvomenthone by direct bromination of carvomenthone, and *1,8*-dibromocarvomenthone by brominating dihydrocarvone in acetic acid + hydrogen bromide. As to the course of the reactions with these isomerides, which were partly investigated in their various optical modifications, differences were noted in their behaviour to aqueous alkalies, depending on the position of the bromine atoms. In these reactions, Wallach noted the following as the main points: —

1. Double-brominated cyclohexanones pass over comparatively easily into phenols by means of aqueous potash solutions under the conditions chosen in those cases, where the two bromine atoms had been added to a double-bond next to the carbonyl group and not separated from the latter by any substituting group.

2. In case the double-bond is vicinal to the carbonyl group, but separated therefrom by a substituting group, the ring is ruptured very easily on treatment with alkalies, with formation of aliphatic ketoacids with equal number of carbon atoms.

3. When the bromine atoms are distributed between nucleus and side-chain, or stand solely in the latter, the reaction can pass off in various ways. A general rule for these very varying possibilities cannot be established.

4. The most interesting results were obtained with those bromides, where the bromine atoms must be assumed to be distributed in the nucleus, next to the carbonyl group. From these hexacyclic bromides one can easily arrive, *viâ* intermediate products, to pentacyclic hydroxycarboxylic acids.

Active dihydrocarvone yields various dibromides, a liquid one, *8,9*-dibromomenthanone-*2*, and a crystalline one, the structure of which is not yet settled. On treating the dihydrocarvone dibromide with aqueous caustic potash, there results, besides a little carvacrol and carvenone as by-products, as main product a heavy brominated oil giving on reduction with zinc and caustic soda solution dihydrocarvone. This experiment, therefore, shows that one of the two bromine atoms of the dibromide is linked very strongly. The crystalline bromide of dihydrocarvone forms on treatment with aqueous potash a hydroxyketone $C_{10}H_{16}O_2$ with only one double-bond, the constitution of which is not yet quite ascertained.

Carvenone dibromide (oily) forms carvacrol on shaking with aqueous potash.

1,2-Dibromomethyl-*1-cyclo*hexanone-*3* (from Δ^1-methyl-*1-cyclo*hexenone-*3* by bromination) passes over into m-cresol on shaking with dilute potash solution.

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[1]) *Liebig's Annalen* **414** (1918), 271.

Carvotanacetone (Δ^6-menthenone-*2*) used for preparing its dibromide (*1,6*-dibromomenthanone-*2*) may be obtained after various methods, in the simpliest way by abstracting hydrogen bromide from monobromocarvomenthone. The dibromide, on shaking with aqueous potash, dissolves nearly entirely, the principal product of the reaction being an acid $C_{10}H_{18}O_3$, δ-acetyl-β-*iso*propyl valeric acid.

1,2-Dibromomenthanone-*3* is obtained by brominating Δ^1-menthenone-*3* from peppermint oil. On shaking with aqueous potash it yields a solid monobromomenthanone-*3*, m. p. 42 to 43°, thymol being formed as by-product. On heating the monobromide alone or with sodium methoxide thymol is obtained. It is noteworthy that the monobromide adds bromine only with great difficulty; it is, therefore, not improbable that the body contains a diagonal bond in lieu of a ethylene bond. At any rate, the constitution of the monobromide is not yet ascertained.

4,5-Dibromomenthanone-*3*, prepared by brominating Δ^4-menthanone-*3*, yields on shaking with aqueous potash a ketonic acid with 10 carbon atoms.

The experimental details on the transformation of hexacyclic ketones into *cyclo*pentanones are to be found in Wallach's[1]) 124th paper "On Terpenes and Essential Oils". In supplementing our abstract[2]) from the short notice on the same subject published in the *Nachrichten der K. Gesellschaft der Wissenschaften,* Göttingen, we add the following. In the nine transpositions of *cyclo*hexanones in to *cyclo*pentanones described by Wallach *viâ* the dibromides of the former, pentacyclic hydroxycarbonylic acids are formed as intermediate products. Nothing is yet established as to the further course of the reaction. At any rate Wallach revokes his former assumption that merely orthoketones are formed which then undergo the benzilic-acid-transposition. On the contrary it may be taken for granted that a rather complicated reaction takes place where the hydroxy ketones primarily assumed or reformed from their isomerides suffer at first a ring-rupture and form acids which by intramolecular condensation pass over into pentacyclic α-hydroxy acids. Such intermediate acids could in some cases be proved to be present, but could not yet purified sufficiently for analysis.

As to the further reaction of the dibromides, an excess of 4 per cent. aqueous caustic potash solution was employed. In case of liquid bromides, or of such reacting easily, shaking with the potash solution was sufficient; the higher melting bromides, however, could be brought to react only with simultaneous heating. For such cases, Wallach employed a copper vessel, the construction of which is illustrated in the original paper by a drawing.

The intermediate hydroxy acid resulting in the treatment of *cyclo*hexanone *viâ* its dibromide into *cyclo*pentanone, m. p. 103 to 104°, proved to be α-hydroxy *cyclo*pentanone carboxylic acid.

The dibromide occurring on bromination of *1,2*-methyl-*cyclo*hexanone, m. p. 42 to 43°, was identical with dibromo-*1,3*-methyl-*1-cyclo*hexanone-*2*.

The acid formed as intermediate product on transforming *1,4*-methyl-*cyclo*hexanone into *1,3*-methyl-*cyclo*pentanone is, in Wallach's present opinion, methyl-*1*-α-hydroxy-*cyclo*pentane-*3*-carboxylic acid; probably, it is formed in various stereoisomeric forms, which would account for the unsharp melting point.

The acid occurring on formation of *1,3*-dimethyl-*cyclo*pentanon-*4* from *1,3*-dimethyl-*cyclo*hexanone-*5*, m.p. 92 to 93°, is a dimethyl-*1,3*-α-hydroxy*cyclo*pentanone-*4*-carboxylic acid.

On transforming trimethyl-*1,3,3-cyclo*hexanone-*5* into trimethyl-*1,3,3-cyclo*pentanone-*5*, an acid $C_9H_{16}O_3$, m. p. 88 to 89°, occurs, which according to Wallach's present statement, is a trimethyl-*1,3,3*-α-hydroxy*cyclo*pentanone-*5*-carboxylic acid.

[1]) *Liebig's Annalen* **414** (1918), 296. — [2]) *Report* **1916**, 127.

For the transformation of menthone into dihydrocamphorophorone, it is not necessary to isolate all the intermediate products in the pure state. It is sufficient to heat the pressed cake of the α- and β-modifications of the compound $C_{10}H_{16}O_2$ directly in an autoclave with potash, then to steam off the unattacked material, to acidify the alkaline residue and to extract with ether; the crude acid thus isolated is brought to solution in the theoretical amount of potash or soda lye, the mixture oxidized with a slight excess of potassium permanganate, sulphuric acid added to neutralize all the alkali, and steam conducted through the liquid (warm owing to the neutralization), which yields nearly pure dihydrocamphorophorone. Both the α- and β-compounds obtained from menthone dibromide, may be regarded as unsaturated hydroxyketones; most probably, they are stereoisomerides of the same compound. The α-isomeride is identical with buchu camphor (= diosphenol). Cusmano[1]), too, had found that on shaking menthone dibromide with potash lye buchu camphor results. Hence, the constitution of the menthone dibromide used is *2,4*-dibromomenthanone-*3*.

On brominating inactive menthone, such as is easily accessible by reducing the natural Δ^1-menthenone-*3* according to Paal and Skita[2]), a liquid inactive dibromide is obtained which on treatment with aqueous potash leads to the same products as are obtained from the active dibromide of the m.p. 79 to 80°. When active crystalline dibromomenthone is boiled with anhydrous sodium acetate in glacial acetic acid solution, a large amount of thymol is the result; but on treating the dibromide with sodium methoxide, a mixture is obtained containing a body $C_{10}H_{16}O_2$, probably an oxide.

In order to prepare tetrahydrocarvone (carvomenthone), one starts from active dihydrocarvone — easily accessible from carvone by the old reduction process —, and from carvenone, for obtaining the inactive preparation. Both of these ketones with one double-linking may be reduced most readily and completely under ordinary pressure by Paal's and Skita's method. The dibromides of tetrahydrocarvone melting at 80 to 80° and 66 to 67° respectively must be considered as the active or inactive forms of dibromo-*1,3*-menthanone-*2*. The active dibromide has formerly been described by Cusmano and Poccianti[3]).

Monobromotetrahydrocarvone[4]), on abstracting hydrogen bromide by means of sodium acetate in glacial acetic acid solution, yields carvotanacetone. As alluded to above, tetrahydrocarvone is the most convenient crude material for the preparation of active and inactive carvotanacetone. On shaking with aqueous potash monobromotetrahydracarvone gives rise to a hydroxyketone. Equally, Kötz and Steinhorst arrived at a hydroxyketone when treating monochlorotetrahydrocarvone with potassium carbonate solution.

The behaviour of the afore-mentioned α- and β-modifications of the body $C_{10}H_{16}O_2$ from menthone dibromide has been described elsewhere by Wallach and E. Grote[5]). In their behaviour towards bromine, both forms are alike, so that for the preparation of the bromides the mixture may be used which is obtained on treating menthone dibromide with potash lye. The results obtained by Wallach on brominating the α-isomeride (= buchu camphor) differ widely from Semmler's[6]) as well as from Cusmano's[7]) statements. When bromine acts on buchu camphor, the properties of the solvent employed and the temperature observed influence the result largely. A monobromide $C_{10}H_{15}BrO_2$, m.p. 77 to 78° is obtained from the mixture of the α- and β-forms of the

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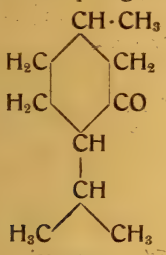
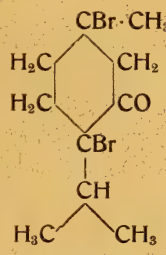
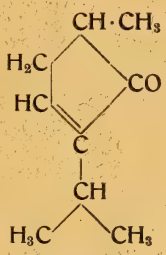
[1]) *Atti R. Accad. dei Lincei* (5) **22**, II (1913), 569; *Chem. Zentralbl.* **1914**, I. 976; *Report* April **1914**, 139. — [2]) *Liebig's Annalen* **397** (1913), 217; *Report* October **1913**, 146. — [3]) *Atti R. Accad. dei Lincei* (5) **23**, I. (1914), 347; *Chem. Zentralbl.* **1914**, II. 481; *Report* April **1915**, 104. — [4]) Comp. Kötz and Steinhorst, *Liebig's Annalen* **379** (1911) 25; *Report* April **1911**, 182. — [5]) *Nachr. K. Ges. Wiss., Göttingen*, meeting of Oct. 26, **1917**. — [6]) *Berichte* **39** (1906), 1158; *Report* October **1906**, 140. — [7]) *Chem. Zentralbl.* **1914**, I. 976; *Report* April **1914**, 139.

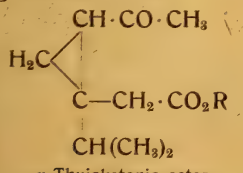
compound $C_{10}H_{16}O_3$ as well as from the pure α-isomeride (buchu camphor) on brominating with one molecule of bromine in glacial acetic acid solution. The bromide may be purified by steam-distillation; doubtless it is identical with the bromide obtained by Cusmano when brominating buchu camphor in chloroform solution, for which, however, he quotes the m.p. 85°. In Wallach's opionion, Cusmano's formula for the monobromide seems to be incorrect. A different bromide of the m.p. 100 to 101°, probably also a monobromide, was obtained from the body $C_{10}H_{16}O_2$ on bromination according to the process described above. It is obtained frequently on brominating in glacial acetic acid solution warmed to 60°, and is not volatile with steam. A dibromide $C_{10}H_{14}Br_2O_2$, m.p. 44 to 45° is obtained either by brominating the monobromide of the m.p. 77° or by the action of an excess of bromine on a solution of the compound $C_{10}H_{16}O_2$; it is then best to work in ethereal solution. The dibromide forms dichroitic green-tinged crystals of the appearance of picric acid. The reaction of the dibromide with alkali is similar to that of menthone dibromide with alkali; primarily, an acid $C_{10}H_{20}O_6$, m.p. 88 to 89°, is formed, probably a hydrate of the formula $C_{10}H_{18}O_5 + H_2O$. On heating the acid for itself or with alkali first water, then carbon dioxide is split off with formation of a ketone $C_9H_{14}O$. This ketone may be prepared in a more simple manner by dry distillation of the acid. The semicarbazone of the ketone melts at 183 to 184°. On treatment with palladium + hydrogen, the ketone yields dihydrocamphorophorone. In all probability, the ketone $C_9H_{14}O$ is identical with pulegenone (Δ^8-methyl-*1-iso*propyl-*3-cyclo*pentenone-*2*), so that there would be a case of transformation of menthone into pulegenone: —

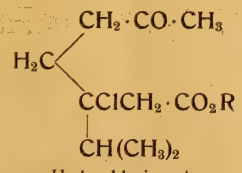

Menthone.

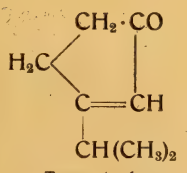

Dibromide.


Pulegenone.

Tanacetophorone. — Some years ago Wallach[1]) communicated the fact that tanacetone dicarboxylic acid, more especially its ester, is easily subject to ring-closure with formation of *iso*propyl-*cyclo*pentenonic ester, which on saponification passes over, with splitting off carbon dioxide, into tanacetophorone. It has now been shown by Wallach and Worlitzer[2]) that tanacetophorone may be prepared from α- or β-thujaketonic acid by a different method. When α- or β-thujaketonic acid is esterified by saturating its alcoholic solution with hydrochloric acid gas, a hydrochloric ester results which by sodium alcoholates may be directly transformed ints tanacetophorone, as is illustrated by the following formulæ: —


α-Thujaketonic ester.


Hydrochloric ester.


Tanacetophorone.

[1]) *Liebig's Annalen* **388** (1912), 49; *Report* October **1912**, 162. — [2]) *Liebig's Annalen* **414** (1917), 220.

The chloro ester is worked up in the crude state as it is nearly impossible to purify it by fractional distillation. When tanacetophorone (*iso*propyl*cyclo*pentenone) is brought to react with methyl magnesium iodide, there results instead of the tertiary alcohol primarily formed, by splitting off of water, in the main the doubly unsaturated hydrocarbon methyl-*1-iso*propyl-*3-cyclo*pentadiene.

On reducing tanacetophorone with palladium and hydrogen, the saturated *1,3-iso*propyl*cyclo*pentanone is obtained, as is well known[1]). This ketone is very sensitive towards alcoholic alkali owing to its great tendency to autocondensation. For preparation of this condensation-product, Wallach treated *iso*propyl*clyco*pentanone with a solution of sodium in alcohol and let the mixture stand for three days in an ice-chest. Here was formed the unsaturated condensation-product $C_{16}H_{26}O_2$ in the crystalline state; m.p. 77 to 78°; semicarbazone, m.p. 192.5°. By reducing this dicyclo*iso*propylpentene-*iso*propylpentanone with palladium and hydrogen, dicyclo*iso*propylpentyl *iso*propylpentanone resulted. The alcohol: dicyclo*iso*propylpentyl *iso*propylpentanol was prepared, by further reduction, from the saturated as well as from the unsaturated ketone.

When the sodium salt of tanacetophorone carboxylic ester is reduced and the solution of the sodium compound of the *iso*propyl*cyclo*pentanone carboxylic ester thus formed is brought into reaction with one molecule of diazobenzene chloride solution, a hydrazone of the melting point 233° is the result.

On bringing *1,3-iso*propyl*cyclo*pentanone in reaction with bromoacetic ester and zinc in benzene solution, there is formed, in addition to the hydroxyester expected, the condensation-product $C_{16}H_{26}O$ from *iso*propyl*cyclo*pentanone dealt with above.

Menthone. — In connection with a paper published some time ago on the synthesis of cyclic ketones[2]), Wallach[3]) describes some experiments on the preparation of compounds containing the *n*-propyl group. It is noteworthy that the combinations with *normal* propyl corresponding to menthone and menthol show an entirely different smell. The primary material for these investigations was Δ^3-methyl-*1-n*-propyl-*4-cyclo*hexene (I) which was prepared from methyl-*1-n*-propyl-*4-cyclo*hexanol-*4* (obtained by Sabatier[4]) from *p*-methyl*cyclo*hexanone) by heating with diluted sulphuric acid. The hydrocarbon thus obtained did not show a quite constant boiling point; the fraction of the b.p. 173 to 176° was worked up. When hydrogen chloride was abstracted from the nitrosochloride (m.p. 134 to 135°) an oxime was formed which on hydrolysis with dilute sulpluric acid gave Δ^4-methyl-*1-n*-propyl-*4-cyclo*hexenone-*3* or Δ^3-methyl-*1-n*-propyl-*4-cyclo*hexenone-*5* (II), a yellow-coloured ketone of the b.p. 220 to 223°; semicarbazone, m.p. 153 to 154°.

By reduction according to Skita in methylalcoholic solution the methylpropylhexenone passes over into methyl-*1-n*-propyl-*4-cyclo*hexanone (*normal* menthone) (III); colourless liquid without the smell of menthone; b.p. 215 to 217°; $d_{19°}$ 0.8960; n_D 1.4511; semicarbazone, m.p. 149 to 152°; oxime, m.p. 87 to 88°. Oxidation which chromic and sulphuric acids leads to a ketonic acid with 10 carbon atoms, thus proving that the oxygen of the carbonyl group is situated in the carbon nucleus and not in the side-chain. The hydrocarbon *1,4*-methyl*cyclo*hexene propane (IV), isomeric with methylpropyl-*cyclo*hexene, may be transformed, *viâ* its nitrosochloride, into the oxime of an unsaturated ketone which on reduction according to Skita passes over into a saturated extracyclic ketone $C_{10}H_{18}O$ (V) of the b.p. 210 to 211°; semicarbazone, m.p. 182 to 183°; oxime,

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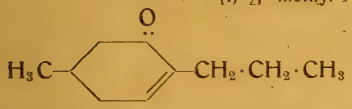
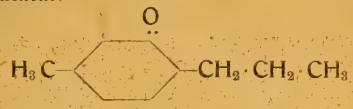
[1]) Wallach, *Liebig's Annalen* **381** (1911), 84; **388** (1912), 59; *Report* October **1911**, 127; April **1912**, 184; October **1912**, 162. — [2]) *Liebig's Annalen* **397** (1913), 181; *Report* October **1913**, 145. — [3]) *Liebig's Annalen* **414** (1917), 212. — [4]) *Chem. Zentralbl.* **1906**, I, 1096.

m.p. 95 to 96°. This extracyclic ketone, therefore, has quite different properties as has *normal* menthone with the oxygen linked to the carbon nucleus.

(I) Δ^3-methyl-*1*-*n*-propyl-*4*-*cyclo*hexene.



(II) Δ^4-methyl-*1*-*n*-propyl-*4*-*cyclo*hexenone-*3*.



(III) Methyl-*1*-*n*-propyl-*4*-*cyclo*hexanone-*3*.

(IV) *1,4*-Methyl*cyclo*hexene propane.

(V) Saturated extracyclic ketone from *1,4*-methyl*cyclo*hexene propane.

Wallach has brought a further proof for the fact that in normal menthone the carbonyl group is linked within the carbon ring. *1,3*-methyl*cyclo*hexanone was transformed into its oxalic ester[1]) and the latter, by means of allyl iodide, into the allyl compound *i*-methyl-*1*-allyl-*4*-*cyclo*hexanone-*3*. On reducing the allyl compound according to Skita a ketone was obtained which proved to be wholly identical with the normal menthone prepared in the manner described above.

E. Boedtker[2]) has published a paper on *menthophenylchloromethane* on which we reported on p. 123 our *Report* **1916**. This compound shows a pronounced asymmetrical structure, so that a great number of stereoisomerides must be expected to exist. Nevertheless, only the one form of the m.p. 140° is hitherto known. With the cyanogen derivative, matters are different. Boedtker[3]) prepared the same by adding an aqueous solution of potassium cyanide to a boiling alcoholic solution of menthophenylchloromenthane. According to the length of boiling different products are formed, all being stereoisomeric modifications of the same menthophenylcyanomethane. Boedtker succeeded in isolating from the mixture with indistinct melting point seven different stereoisomeric forms which all differed from each other by their melting points. When the reaction lasts only a short time a yellow labile body of m.p. 193° is obtained which passes over, *viâ* several other labile forms, into the stable modification of m.p. 201°.

Transformation of *menthone* into *pulegenone* has been described by Wallach, see p. 129 of this *Report*.

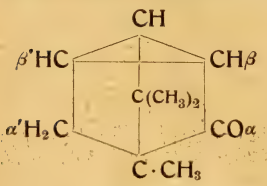
*Peri*cyclo*camphanone*. — On p. 98 of our *Report* April **1915** we discussed a preliminary communication of W. Holz[4]) on *cyclo*camphanone and on Angeli's camphenone. J. Bredt and W. Holz[5]) now report on preparation, properties, and derivatives of *cyclo*camphanone which they term "β-peri*cyclo*camphanone" (I). They have adopted the term "pericyclo" for the trimethylene ring because the "corner" carbon atoms β-β', whose linking closes the tricyclic ring, are in the same proportion to each other as are the "peri" carbon atoms in the hydronaphthalene nucleus.

[1]) Comp. A. Kötz and L. Hesse, *Liebig's Annalen* **342** (1905), 306; *Report* April **1906**, 126. — [2]) *Bull. Soc. chim. IV.* **17** (1915), 374. — [3]) *Ibidem IV.* **23** (1918), 64. — [4]) *Zeitschr. f. angew. Chem.* **27** (1914), I. 347. — [5]) *Journ. f. prakt. Chem.* II. **95** (1917), 133.

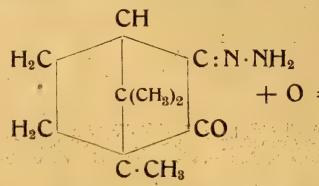
For the preparation of β-peri*cyclo*camphanone the authors start from campher quinone which by heating with hydrazine hydrate is transformed into camphor quinone monohydrazone (II), furnishing principally the α-modification of m.p. 198°. The β-form melts at 103°. Both hydrazones pass over, by means of mercuric oxide in benzene, into diazocamphor (III), m.p. 74 to 75°. The latter, when mixed with copper-bronze powder, furnishes on dry distillation peri*cyclo*camphanone in varying yield; smell, mild of camphor; m.p. 166 to 168°; b.p. 205 to 207°; semicarbazone, m.p. 243 to 244°. On treatment, in a sealed bottle, with an excess of hydrobromic + glacial acetic acid the ketone passes over into β-peri*cyclo*camphanone hydrobromide, m.p. 113 to 114° which on reduction with zinc dust and glacial acetic acid yields camphor.

On adding bromine to his "camphenone" (taken as unsaturated), Angeli believed a dibromide to result. Bredt and Holz, however, obtained on working according to Angeli's directions merely unattacked *cyclo*camphanone. On the other hand, a dibromide is formed on dissolving *cyclo*camphanone in carbon disulphide, adding one molecule bromine and exposing the solution, in a sealed tube, to direct sun-light for several weeks. The dibromide melted at 56 to 58° and showed the properties stated by Angeli for his dibromide.

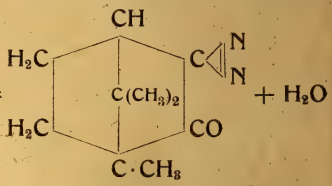
When β-peri*cyclo*camphanone is heated with hydrazine hydrate and alcohol in a sealed tube, β-peri*cyclo*camphanone hydrazone (V) is the result; m.p. 45°; b.p. 143 to



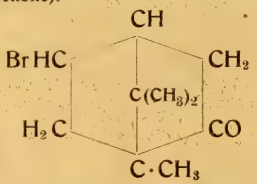
(I) β-Peri*cyclo*camphanone (Camphenone).



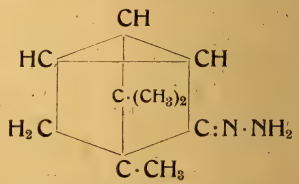
(II) Camphor quinone hydrazone.



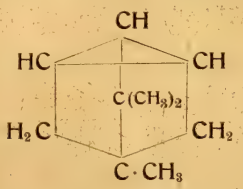
(III) Diazocamphor.



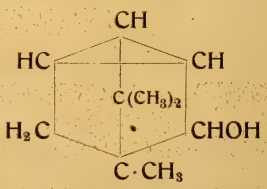
(IV) β-Peri*cyclo*camphanone hydrobromide.



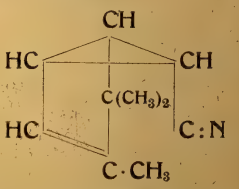
(V) Peri*cyclo*camphanone hydrazone.



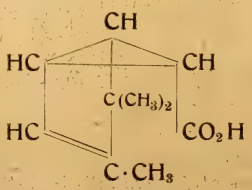
(VI) β-Peri*cyclo*camphane.



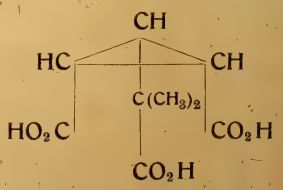
(VII) Peri*cyclo*camphanol.



(VIII) *Cyclo*campholenic nitrile.



(IX) *Cyclo*campholenic acid.



(X) Cyclo*iso*camphoronic acid.

148° (13 mm.). By heating the hydrazone with sodium and alcohol in a sealed tube, β-peri*cyclo*camphane (VI) is obtained; m.p 117 to 118°, b.p. 150 to 152°. This hydrocarbon is even more volatile than camphane; on keeping in closed glass vessels it sublimed on the walles in shape of clear tetrahedrie crystals.

By means of sodium and alcohol, β-peri*cyclo*camphanone could be reduced to β-peri*cyclo*camphanol (VII); m.p. 174 to 176°, b.p. 205 to 208°; phenylurethane, m.p. 106 to 108°, methylxanthate, m.p. 49 to 51°, chloride, m.p. 130°; methyl ether, b.p. 79 to 80° (16 mm.), 189° to 190° (ord. pressure). The molecular refraction of β-peri*cyclo*camphanol methyl ether was 48.8156, calculated for $C_{11}H_{18}O<$,48.041. The difference, 0.77, points to the presence of a tricyclic ring which, according to recent observations, causes an exaltation of + 0.65 to + 0.85.

The oxime op β-peri*cyclo*camphanone was prepared according to the method approved with camphor oxime. Since its melting point was indefinite it may probably be the case of stereoisomerides. On treatment with dilute sulphuric acid, the oxime passes over into *cyclo*campholenic nitrile (VIII), a viscid, paraffine-like mass melting at 78 to 80°. The saponification of the nitrile to the acid (IX) was effected only with difficulty, the best method being heating with a 25 per cent. solution of caustic potash in a sealed tube to 100° for some time. The acid melts at 108 to 110°. By heating the silver salt with ethyl iodide, Bredt and Holz obtained the ethyl ester; b.p. 111 to 112° (14.5 mm.). Oxidation of *cyclo*campholenic acid with potassium permanganate or chromic acid mixture led to cyclo*iso*camphoronic acid (X), a body crystallizing in small colourless scales of the m.p. 228 to 230°.

Camphenilone. — S. S. Nametkin, E. A. Grekova, and A. M. Chuchrikova[1]) hare investigated the oxidation of this ketone. It was very stable towards oxidizing agents, the only definite oxidation product yet obtained being oxalic acid. When camphenilone, however, is heated with dilute nitric acid in a sealed tube to 140 to 150°, there result as oxidation-products crystals of the m.p. 90 to 92°, an oil, and *iso*camphoronic acid; possibly, the crystals and the oil are tertiary nitroketones. The formation of *iso*camphoronic acid was to be expected on account of the accepted formula for camphenilone. The first oxidation-product is probably an α-nitroketone which is then hydrolysed and subsequently oxidized.

Fenchone. — Semmler's[2]) formula for fenchone is now generally accepted, since the reactions of this body are most easily explained thereby. An unobjectionable synthesis of this ketone had hitherto not been carried out, although this was neccessary as a proof for the correctness of Semmler's formula, fenchone being cherecterized by great lability, and well-cheracterized derivatives, such as camphoric acid from camphor, have not been obtained from fenchone.

Only now L. Ruzicka[3]) has succeeded in verifying Semmlers's fenchone formula by total synthesis.

At first, he tried to start from a methyl*cyclo*pentanonic acid, a product of the splitting up of β-fencholenic acid; the structure of the latter acid is well-known, since it yields, on ozonisation, the above-mentioned methyl*cyclo*pentanone carboxylic acid which in its turn, on oxidation, passes over into α-methylglutaric acid, thus revealing its structure.

In case this ketonic acid would be accessible by synthesis, this would form a smooth way for arriving at the synthesis of fenchone, since from the ester of the ketonic acid

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[1]) *Journ. Russ. phys.-chem. Soc.* **48** (1916), 453; *Journ. chem. Soc.* **112** (1917), I. 151. — [2]) *Chem. Ztg.* **29** (1905), 1313; *Report* April **1906**, 124. — [3]) *Berichte* **50** (1917), 1362.

the still unknown homofenchonic acid (corresponding to homocamphenic acid) might be obtained by condensation with ethyl α-bromo*iso*butyrate. Now, homofenchonic acid is a methylcamphenic acid which when distilling its lead salt should pass over into α-methylcamphenilone, *i.e.* fenchone of Semmler's formula, in the same way as lead camphenate yields camphenilone. Homofenchonic acid was comparatively easy to prepare, but the distillation of the lead salt yielded principally a mixture of hydrocarbons with inconstant boiling point.

Ruzicka was, however, successful in transforming methyl *nor*camphor into fenchone by methylation. Methyl *nor*camphor, hitherto unknown, originated, in good yield, from methyl *nor*homocamphoric acid which was obtained by condensing methyl *cyclo*pentanone carboxylate with ethyl bromoacetate. After treating methyl *nor*camphor twice with sodium amide and methyliodide, it furnished, in addition to another hitherto unknown intermediate product, designable as fenchosantenone, pure *r*-fenchone. Fenchosantenone could be separated from fenchone on account of its easier formation of a semicarbazone.

For the formation of *1*-methyl-*3*-keto-*1-cyclo*pentane carboxylic acid the author started from ethyl levulate (I) which was obtained, with a good yield, on boiling the solution of the acid in absolute alcohol for 24 hours with absolute alcohol saturated with hydrochloric acid gas. When treated with ethyl bromoacetate and zinc according to the directions of P. Duden and R. Freydag[1]), levulic ester furnished a lactonic ester, the lactone of *2*-methyl-*2*-hydroxyadipic ester (II). This lactonic ester yielded, on heating with potassium cyanide to 240 to 250°, ethyl *2*-methyl-*2*-cyano-*1,4*-butanedicarboxylate (III). This product is heated with alcoholic sulphuric acid for obtaining ethyl *2*-methyl-*1,2,4*-butanetricarboxylate (IV). For this purpose, the lactonic ester is heated with 1½ mols. potassium cyanide for about 8 hours to 200 to 220° and the product of this reaction boiled for 10 days in an oil-bath heated to 120° with a mixture of concentrated sulphuric acid and alcohol. The tricarboxylic ester (IV) is then boiled in benzene solution with sodium in order to obtain *1*-methyl-*3*-keto-*cyclo*pentane carboxylate (V); the sodium dissolves rapidly, and the slightly coloured solution is poured, after cooling, on ice-water, shaken with dilute sulphuric acid, the solvent removed completely and residual oil, dissolved in benzene, then boiled with hydrochloric acid of medium concentration. In the beginning, strong evolution of carbon dioxide is noticed. The aqueous solution is extracted with ether. *1*-Methyl-*3*-keto-*1-cyclo*pentane carboxylic acid boils at 170° (12 mm.); semicarbazone, m.p. 189 to 190°; ethylate, b.p. 115° (12 mm.).

By heating the ketonic ester (V), in benzene solution, with ethyl α-bromo*iso*butyrate and zinc, ethyl hydroxyhomofenchonate (VI), b.p. 171 to 173° (12 mm.), is obtained. As by-product, dehydrohomofenchonic ester (VII) is formed.

The hydroxyester, even after repeated heating with potassium hydrogen sulphate, yields a product of inconstant boiling point; abstraction of water is performed more evenly by treatment with phosphorus tribromide in chloroform solution. The dehydrohomofenchonic ester thus obtained (VII) boils at 152 to 153° (12 mm.). The acid resulting from saponification of the ester is probably a mixture of two acids of the m.p. 176 to 177 and 110 to 111°.

In consequence of steric hindrance neither the dehydrofenchonic ester nor the acids could be reduced in aqueous-alcoholic or in glacial acetic acid solution by colloidal palladium, under atmospheric pressure, according to Skita. With platinum black in glacial acetic acid (method of Willstätter), however, the hydrogenization was effected. Ethyl homofenchonate (VIII) boiled at 150 to 155° (13 mm.). The free acid, a mixture,

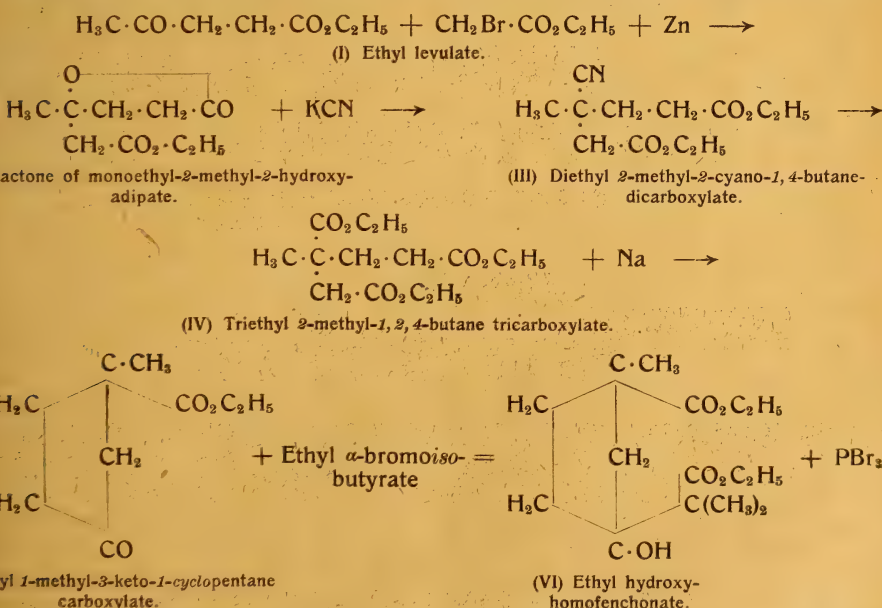
[1]) *Berichte* **36** (1903), 953.

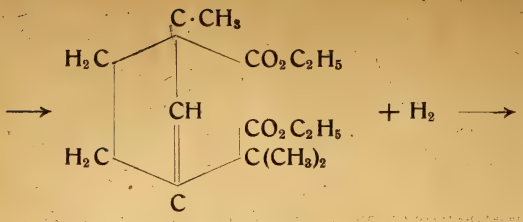
could not be split up by recrystallization from water. On distilling the lead salt of the acid, traces of fenchone are perhaps formed, since from the reaction-product an oxime, m.p. 156 to 157° was obtained, which after mixing with (*d* + *l*) fenchone oxime, m.p. 158°, melted at 157°. But hydroxylamine hydrochloride, m.p. about 155°, gave no depression in the m.p. after mixing with fenchone oxime, so that it is doubtful whether fenchone had been formed on distilling the lead salt.

For preparing ethyl dehydromethyl*nor*homocamphorate (IX) ethyl methyl*cyclo*pentanone carboxylate (V) is brought, in benzene solution, to react with zinc and ethyl bromoacetate. The product resulting is a mixture of the dehydro ester (IX) and the hydroxy ester (X). In order to transform the mixture entirely into the unsaturated ester it is treated with phosphorus trichloride in chloroform solution. The dehydro ester is then reduced, according to Willstätter, in ethereal solution with platinum black and hydrogen. The resulting ethyl methyl*nor*homocamphorate (XI) boils from 147 to 149° (14 mm.). The free acid, after recrystallization from water, melts from 116 to 118°. In addition, an isomeric acid seems to be present which crystallizes more difficultly.

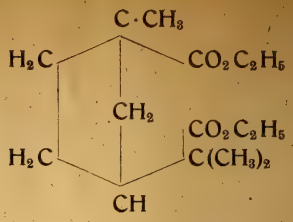
The lead salt of methyl*nor*homocamphoric acid yields on dry distillation methyl-*nor*camphor (XII), a liquid, the semicarbazone of which melts at 210 to 211°. Methyl-*nor*camphor was brought into reaction with methyl iodide and sodium amide in absolute-ethereal solution. The reaction-product, freed from excess of methyl iodide and solvent, was treated with semicarbazide hydrochloride and sodium acetate in methylalcoholic solution. The mother-liquor of the semicarbazone was distilled with steam, whereby fenchone was removed. After recrystallizing the semicarbazone melted at 208 to 209°; the fenchosantenone (XIII) regenerated therefrom was a liquid with a smell of fenchone; oxime, m.p. 98 to 99°.

The *r*-fenchone (XIV) distilled off from the semicarbazone of fenchosantenone boiled at 72 to 73° (12 mm.). The oxime, m.p. 158 to 159°, showed after mixing with the equal amount of (*d* + *l*)-fenchone oxime, m.p. 158 to 159° (prepared from *d*-fenchone oxim from fennel oil and *l*-fenchone oxim from thuja oil) no depression of the melting point.

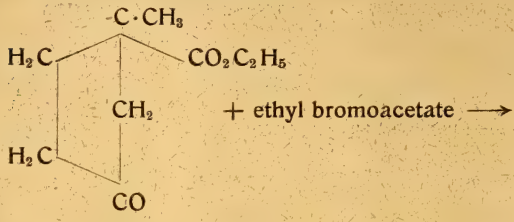




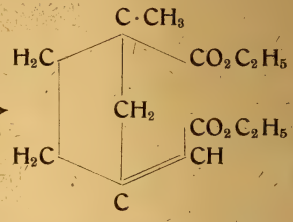
(VII) Ethyl dehydrohomofenchonate.



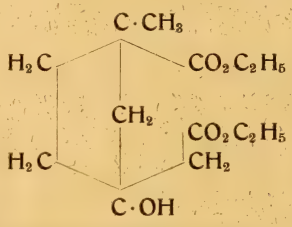
(VIII) Ethyl homofenchonate.



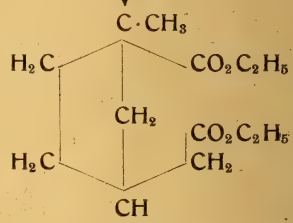
(V) Ethyl *1*-methyl-*3*-keto-*1*-*cyclo*pentane carboxylate.



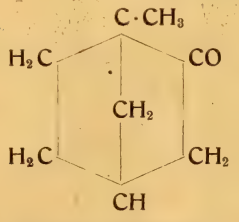
(IX) Ethyl dehydromethyl*nor*homocamphorate.



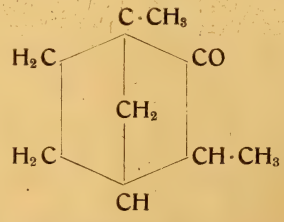
(X) Ethyl hydroxymethyl*nor*homocamphorate.



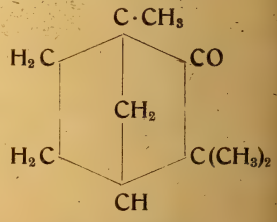
(XI) Ethyl methyl*nor*homocamphorate.



(XII) Methyl*nor*camphor.



(XIII) Fenchosantenone.



(XIV) Fenchone.

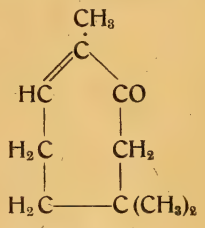
Pulegone. — On p. 127 of our *Report* **1916** we took notice of the autoxidation of pulegone performed by E. Sernagiotto[1]) under the influence of light. The authors has now[2]) published details about this oxidation. Pulegone was exposed to light for four month in bottles filled with oxygen, in presence of some water, and the reactionproduct then distilled with steam. The distillate contained acetone, formic acid, and traces of higher fatty acids. The recidual liquid, after shaking with sodium carbonate solution gave on extraction with ether a crystalline lactone of a ketonic acid $C_{10}H_{14}O_3$, m. p. 183.5°; oxime, m. p. 116°. On oxidation with chromic acid, the lactone yielded β-methylglutaric

[1]) *Atti R. Accad. dei Lincei* (5), **24** (1915), 1065; *Chem. Zentralbl.* **1916**, I. 1147. — [2]) *Gazz. chim. ital.* **47** (1917), I. 150; *Journ. Soc. chem. Industry* **36** (1917), 613.

acid, m. p. 86.7°, and a small amount of acetone. The alkaline liquid contained an acid of the composition of β-methyladipic acid (m. p. 84°) and an acid $C_{10}H_{18}O_5$ of unknown constitution.

Carvone. — Some years ago, Ciamician and Silber[1]) had stated that on exposition to light of carvone, contrary to the usual course of such reaction, no acid products are formed, but a ketone isomeric with carvone, which strongly resembled camphor. This ketone has now been investigated closely by E. Sernagiotto[2]) who termed it *carvone-camphor*. On oxidation with alkaline permanganate solution the ketone furnished a dibasic acid $C_{10}H_{14}O_4$, m. p. 174°, and a monobasic ketonic acid $C_9H_{12}O_3$, m. p. 196°. When carvone-camphor is left for several days in contact with alcoholic sulphuric acid and the product distilled with steam, a liquid isomeride is obtained, *iso*carvone-camphor, b. p. 222 to 224°; oxime, m. p. 167°; semicarbazone, m. p. 209°. By reduction of carvone-camphor with sodium and alcohol the corresponding alcohol carvone-borneol is formed, m. p. 135°, the semicarbazone (?!) of which melts at 239°.

Eucarvone. — As Wallach[3]) has demonstrated shortly ago, there is obtained, by reduction of eucarvoxime with hydrogen according to Paal or Skita, a hitherto unknown β-dihydroeucarvoxime, m. p. 122 to 123°, and on further reduction an also new tetrahydroeucarvoxime, m. p. 56 to 57°. In his 125th paper "On Terpenes and Essential Oils" Wallach[4]) occupies himself anew with derivatives of the eucarvone series. He found that the unsaturated β-dihydroeucarvoxime could be reduced direct to the saturated base tetrahydroeucarvylamine, in accord with the formula accepted formerly for β-dihydroeucarvone. The reduction of the oxime was effected by means of sodium and alcohol. The acetyl compound of the base melted at 110.5° and was identical with the acetyl derivative of tetrahydroeucarvylamine obtained by Wallach on reducing tetrahydroeucarvoxime.



β-Dihydroeucarvone.

Wallach has furthermore studied the chemical behaviour of tetrahydroeucarvone. On brominating with bromine in glacial acetic acid solution, with ice-cooling it yields monobromotetrahydroeucarvone, m.p. 32°, which on shaking with potash solution passes over into monohydroxytetrahydroeucarvone; semicarbazone m. p. 193°; oxime, m. p. 84°. On reduction with sodium in alcoholic solution, the hydroxyketone furnishes a glycol, b. p. 112 to 117° (4 mm.). The hydroxyketone forms a chromic acid ester of high resistance. On brominating tetrahydroeucarvone in glacial acetic acid without cooling, a dibromide, m. p. 68°, is obtained which on treatment with aqueous potash yields a saturated monobasic acid of m. p. 91.5 to 92.5°. When the dibromide is thought to react with sodium methoxide an oil with the smell of cloves is the result, nothing, however, being yet known as to the nature of this body; probably, it is an oxide.

Phenols and phenol ethers.

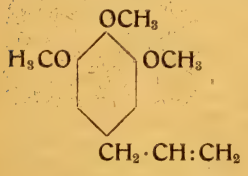
Concerning the p-*nitrobenzyl ethers* of various phenols, see p. 92 of this *Report*.

Methyl chavicole. — During a research on Javanese basil oil P. van Romburgh[5]) had studied the products of polymerisation obtained from methylchavicole on heating in

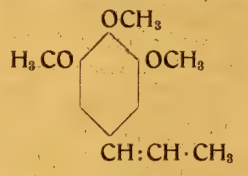
[1]) *Berichte* **41** (1908), 1928; *Report* November **1908**, 159. — [2]) *Gazz. chim. ital.* **47** (1917), I. 153; *Journ. Soc. chem. Industry* **36** (1917), 614. — [3]) *Liebig's Annalen* **403** (1914), 87; *Report* April **1914**, 143. — [4]) *Ibidem* **414** (1918), 367. — [5]) *K. Akad. Wetensch., Amsterdam* **1909**, 15; *Report* October **1909**, 26.

sealed tubes up to 250° for 48 hours, when the formation of two products, m. p. 98° and 166° was observed. These compounds have now been investigated by the author in community with J. M. van der Zanden[1]). The body of the m. p. 166° forms a dibromide of the m. p. 139°. The compound of the m. p. 98° when oxidized with potassium permanganate in acetone solution yields, in addition to anisic acid, an acid $C_{12}H_{16}O_3$, m. p. 113° which could be oxidized further to an acid of the m. p. 138°. Oxidation of the compound m. p. 166° led merely to anisic acid. Amongst the polymerisation-products of methylchavicole, the authors found furthermore *p*-tolyl methyl ether (= *p*-cresol methyl ether).

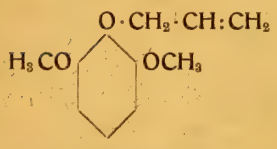
Elemicin. — This body is, according to Semmler's[2]) discovery, the principal constituent of Manila elemi oil, for which that investigator established the formula of *4*-allyl-*1,2,6*-trimethoxybenzene (I). On heating elemicin with sodium or boiling with alcoholic potash, *iso*elemicin, *4*-propenyl-*1,2,4*-trimethoxybenzene (II) results, which is isomeric in its structure with asarone. F. Mauthner[3]) has now succeeded in synthesizing both of these bodies. He heated dimethylpyrogallic ether and allyl bromide, dissolved in acetone, for eight hours on the water-bath with reflex condenser with potassium carbonate. The result is *2,6*-dimethyl-*1*-allylpyrogallic ether (III), a colourless, limpid oil, b. p. 140 to 141° (14 mm.). On heating, this allyl ether suffers a rearrangement insofar as the allyl group attaches itself to the benzene nucleus[4]) with formation of *4*-hydroxy-*3,5*-dimethoxy-*1*-allylbenzene (IV), b. p. 168 to 169° (11 mm.). This body was then methylated with caustic soda and dimethyl sulphate, when *3,4,5*-trimethoxyallylbenzene, elemicin (I), was formed. In order to ascertain the position of the side-chain, Mauthner oxidized the synthetical product with potassium permanganate and obtained thus trimethylgallic acid, m. p. 167°. Since this was the only product of the oxidation, the position of the side-chain was established. For proving the position of the double-bond Mauthner oxidized the synthetical body with ozone, this resulting in trimethyl homogallic aldehyde. In order to obtain *3,4,5*-trimethoxypropenylbenzene (*iso*elemicin) from *3,4,5*-trimethylallylbenzene the latter was warmed for 24 hours with alcoholic potash. Oxidation of this synthetical *iso*elemicin with ozone yielded trimethylgallic aldehyde.



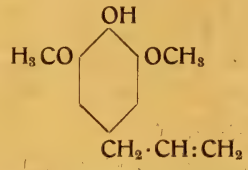
(I) Elemicin.



(II) *Iso*elemicin.



(III) 2,6-Dimethyl-1-allyl pyrogallic ether.



(IV) 4-Hydroxy-3,5-dimethoxy-1-allylbenzene.

Acids.

d-*Benzylidene campholic acid.* — Campholic acid (tetramethyl-*1,2,2,3-cyclo*pentane *3*-carboxylic acid) is known since a long time, benzylidene campholic acid, on the contrary, has been described only in 1900 by Haller and Minguin[5]). As has now been

[1]) *K. Akad. Wetensch., Amsterdam* **20** (1917), 64; *Journ. chem. Soc.* **112** (1917), I. 690. — [2]) *Berichte* **41** (1908), 1768, 1918, 2183, 2556; *Report* October **1908**, 50. — [3]) *Liebig's Annalen* **414** (1917), 250. — [4]) The interesting transposition of phenyl allyl ethers into C-allyl phenols has been described some time ago by L. Claisen (*Berichte* **45** [1912], 3157; *Liebigs Annalen* **401** [1913], 21; *Report* April **1913**, 144; April **1914**, 145). — [5]) *Compt rend.* **130** (1900), 1362.

found, however, these investigators had not benzylidene campholic acid in hand, but a mixture of other bodies. H. Rupe and A. Blechschmidt[1]), namely, considered that acid to be specially suited for studying the influence of the constitution on the optical rotation of organic bodies, and they endeavoured to synthesize the acid following the directions of Haller and Minguin. On acting with glacial acetic + hydrobromic acid in the heat on benzylidene camphor these authors had obtained phenylhydroxyhomocampholic and benzylidene campholic acids which were separated by treatment with alcohol. The hydroxy acid is a well-crystallizing substance, the alleged benzylidene homocampholic acid, however, is described as an uncrystallizable glassy mass melting indistinctly at about 100°. This behaviour appeared to Rupe and Blechschmidt not to agree with the structure of such a compound. They repeated, therefore, the work of Haller and Minguin and obtained actually a mixture consisting of phenyl hydroxy campholic acid and that glassy acid. They succeeded in separating the two acids by means of the magnesium salts and found that the glassy acid consisted, for the greater part, of phenyl hydroxy campholic acid, a minor part being a wax-like body of unknown composition and a small amount of an acid which according to its properties could by no means be identical with benzylidenecampholic acid. Consequently, this latter acid had hitherto not been prepared and was unknown, but it was easily arrived at by dehydration when boiling phenyl hydroxy campholic acid with commercial formic acid. *d*-Benzylidene campholic acid is a well-crystallizing substance of the m. p. 124 to 125°; b. p. 228° (11 mm.). Its structure is manifested by the results of the oxidation with permanganate, *i. e.*, benzoic and camphoric acids:—

$$\underset{\text{Benzylidene campholic acid.}}{C_8H_{14}\begin{matrix}CH{:}CH\cdot C_6H_5\\ CO_2H\end{matrix}} + 4\,O = \underset{\text{Camphoric acid.}}{C_8H_{14}\begin{matrix}CO_2H\\ CO_2H\end{matrix}} + \underset{\text{Benzoic acid.}}{C_6H_5CO_2H}$$

Benzylidene camphoric acid, being unsaturated adds 2 atoms bromine or 1 mol. hydrobromic acid. The hydrobromide obtained hereby (monobromobenzyl campholic acid) results also from benzylidene camphor on prolonged standing with glacial acetic + hydrobromic acids. According to Haller and Minguin, bromobenzyl camphor should be obtained thereby, but Rupe and Blechschmidt were unable to arrive at this body from benzylidene camphor in this manner.

Reduction of *d*-benzylidene campholic acid with hydrogen in presence of nickel or colloidal palladium yielded *d*-benzyl campholic acid, m. p. 119 to 119.5°.

Camphoric acid. — In a paper on the salts and esters of *d*-camphoric acid, H. Thoms and P. Runze[2]) report on a noteworthy behaviour of this acid. When 5 g. *d*-camphoric acid are dissolved in 190 ccm. hot water and this solution gradually mixed with an aqueous solution of 3.58 g. (= ½ mol. $Na_2CO_3 + 10\,H_2O$) sodium carbonate, subsequent repeated shaking out with ether of the chilled solution yielded 2.37 g., *i. e.*, nearly one-half of the acid employed could be recovered, the other half remaining dissolved in the aqueous solution as neutral sodium camphorate. Also when working in the reverse order, *i. e.*, on adding the solution of camphoric acid to the sodium carbonate solution, or when working in the cold by triturating the acid with ½ mol. $Na_2CO_3 + 10\,H_2O$ with cold water on a shaking-machine and extracting by ether — in all cases nearly one-half of the camphoric acid taken in reaction can be shaken out with ether. It was an interesting point to ascertain how the acid esters

[1]) *Berichte* **51** (1918), 170. — [2]) *Berichte* **50** (1917), 1217.

of camphoric acid would behave concerning the formation of salts, as several acid phenol esters of camphoric had to be tested for therapeutical use.

For the preparation of mono-*o*-cresyl camphorate *o*-cresol was dissolved in twelve times its weight of xylene, 1 mol. powdered sodium hydroxide added until sodium *o*-cresate was formed, and the whole shaken, after addition of 1 mol. camphoric anhydride, on the shaking-machine. The gelatinous mass separated off is dissolved in water, acidulated with diluted sulphuric acid and the acid ester extracted with ether. After drying the ethereal solution with calcium chloride the ether was evaporated in a vacuum desiccator and the ester recrystallized from diluted alcohol. It formed glistening needles, m. p. 127°. The mono-*m*-cresyl camphorate obtained by the same method melted at 102 to 103°.

Attempts to arrive at the potassium or sodium salts of mono-*o*-cresol camphorate by neutralizing the acid ester with potash or soda lye proved unsuccessful; neither was it possible to separate the sodium salt by adding the calculated amount of sodium methoxide or ethoxide, dissolved in alcohol, to an alcoholic solution of the acid ester. By titrating this ester with alcoholic decinormal potash solution it could be proved that the free carbonyl group of the acid ester was saturated by alkali. In consequence of the strong tendency of camphoric acid to form neutral salts, evidently when neutralizing the acid *o*-cresol ester of the acid with potash or soda solution a decomposition of the ester takes place in this manner that first the phenol radical is split off by the alkali, and then neutral camphorate is formed besides free camphoric acid.

Owing to the weak basic properties of ammonia, an ammonium salt could be prepared. On adding alcoholic ammonia to a solution of the ester in alcohol + ether the ammonium salt was thrown down in form of a finely-powdered white precipitate. In addition, the following derivatives were obtained: — cupri salt of mono-*o*-cresyl *d*-camphorate, the methylamine and diethylamine salts of the acid *o*-cresyl *d*-camphorate.

In common with G. K. W. Zehrfeld, Thoms[1]) has studied this remarkable behaviour of *d*-camphoric acid from the physico-chemical point of view; they endeavoured to elucidate the neutralization process on physical lines by measuring the conductivity. By this method they proved that acid salts of camphoric acid actually exist, whereas the experiments dealt with above might justify the conclusion that such salts were altogether unable to exist.

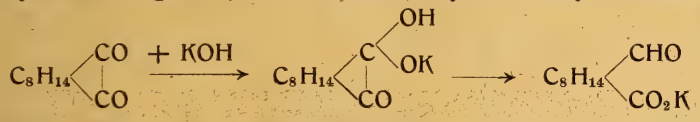
From the aqueous solution of the sodium salt also of l-*iso*camphoric acid Thoms and Th. Sabalitschka[2]) were able to prove that a part of the acid present could be extracted with ether. These processes pass off in harmony with the laws of chemical equilibrium, chemical mass-action, and chemical statics. The fission of the acid salt, in aqueous solution, into neutral salt and free acid takes place in presence of water which according to the current views can only play the part of a dissociating solvent. The authers believe to be justified in assuming that the partial rearrangement of the acid salt into neutral salt and free acid depends upon a different uniting of the free ions so as to form new bodies. It is beyond our scope to explain these theoretical views to our readers. We wish to point out that in the experimental part of this publication the following is dealt with: — the scission of the acid sodium salt of l-*iso*camphoric acid, in aqueous solution, into neutral salt and free acid; the same reaction with the acid sodium salts of phthalic and of *iso*phthalic acids; the behaviour of the aqueous solutions of the acid potassium salts of oxalic and sulphuric acid;

[1]) *Berichte* 50 (1917), 1221. — [2]) *Ibidem* 1227.

finally, the same behaviour of the acid ammonium, lithium, sodium, and potassium salts of *d*-camphoric acid.

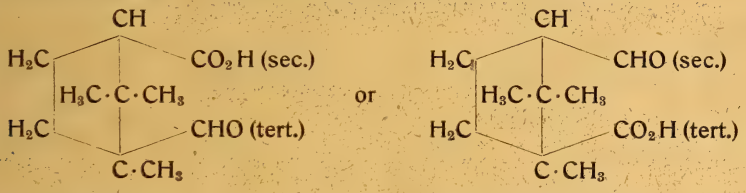
Camphoceanaldehydic acid. — In a comparatively simple manner, *i. e.*, by fusing camphor quinone with aqueous potash solution, J. Bredt[1]) succeeded in preparing the semi-aldehyde of camphoric acid, camphoceanaldehydic acid (sec.-tert.). The semi-aldehydes of phthalic, succinic, naphthalic, glutaric and other dibasic acids are known since some time, but it had not yet been possible to obtain the corresponding reduction-product of camphoric acid. This ready formation of the semialdehyde of camphoric acid from camphor quinone was by no means to be expected, since Claisen and Manasse[2]) had obtained soleby camphoric acid by splitting up this quinone by means of alcoholic potash solution.

Possibly, the first product resulting from fusing camphor quinone with potash is an additive intermediate combination of the quinone with potassium hydroxide, which is easily split up by water. This unstable addition-product might then be rearranged, by atomic migration, into the semialdehyde of camphoric acid: —



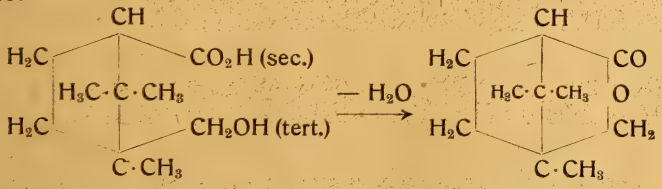
Camphor quinone. Intermediate product. Semialdehyde of camphoric acid.

Furthermore, the question had to be solved which of the two aldehydoacids admitted by Bredt's formula for camphoric acid was present and whether the aldehyde radical was linked to a secondary or tertiary carbon atom of the nucleus: —



Camphoceanaldehydic acid (tert.-sec.). Camphoceanaldehydic acid (sec.-tert.).

Decision was brought about by means of electrolytical reduction of the aldehydic acid, and that in favour of the tert.-sec. formulation. The result was a tert.-sec. hydroxy carboxylic acid, hydroxy campholic acid, when on abstracting water passed over into *β*-campholide: —



Hydroxycampholic acid. *β*-Campholide.

β-Campholide differs from *α*-campholide, *inter alia*, by remaining unchanged when treated with glacial acetic + hydrobromic acid, *α*-campholide being hereby split up to bromocampholic acid, with addition of hydrogen bromide: —

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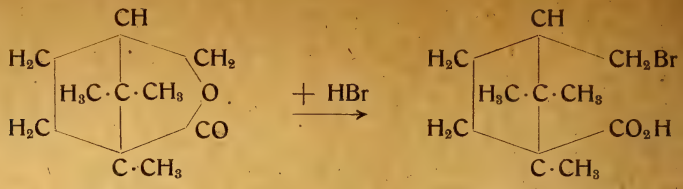
[1]) *Journ. f. prakt. Chem.* II. **95** (1917), 63. — [2]) *Liebig's Annalen* **274** (1893), 86.



α-Campholide. Bromocampholic acid.

For preparing inactive camphor quinone Bredt started from (*d* + *l*)-*iso*nitroso-camphor, which was obtained from inactive camphor by treatment, in benzene solution, with sodio-potassium amide and subsequently, while cooling, with amyl nitrite. The solution of *iso*nitrosocamphor in glacial acetic acid was trented with powdered sodium hydrogen sulphite for transformation into camphor quinone. After boiling the mixture on a sand bath beneath a reflux condenser hydrochloric acid was added and the mixture heated anew. The (*d* + *l*)-camphor quinone resulting hereafter was recrystallized from alcohol; m. p. 199°.

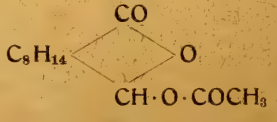
In order to obtain camphoceanaldehydic acid 15 g. of the quinone were heated with a solution of 45 g. potassium hydroxide in 45 ccm. water up to 280 to 290° so long until the colour of the mixture (in the beginning yellow) *viâ* pale yellow and violet, had turned brown. This process lasted 40 minutes. The reaction-product is then dissolved in water and sulphur dioxide passed into the solution, unchanged quinone being extracted by means of ether. Some of the aldehydo acid passes over into the ether and may be regained by shaking with sodium carbonate solution. The liquid, after saturation with sulphurous acid, is supersaturated with sulphuric acid and extracted with ether for isolating the aldehydic acid which after recrystallization from ether melted from 61 to 64°. The indistinct melting point indicates that the aldehydic acid exists in a *cis*- and a *cis-trans*-modification, as does camphoric acid.

The acid, and more especially its solutions, oxidises on standing at the air readily to camphoric acid. The best is to prepare at once suitable derivatives, such as the semicarbazone, oxime, or lactone, which may equally be prepared when the acid is contaminated with camphoric acid. The acid proved to be optically inactive.

d-Camphoceanaldehydic acid from the quinone of Japanese camphor, purified by means of its acetate and recrystallized from ether, at 76 to 78°. Here, too, it may be assumed that the indistinct melting point indicates the presence of two stereo-isomeric forms. $[\alpha]_{D18°} + 80°25'$ (in methyl alcohol; c = 10.586); $[\alpha]_{D18°} + 103.01°$ (in benzene; c = 8.265).

The oxime of the aldehydic acid was obtained when adding hydroxylamine hydrochloride to the aqueous solution of the acid. The *d*-oxime melted at 153 to 155°, the inactive oxime at 148 to 149°, the latter being formed far more difficultly than the active form. The semicarbazone of the d-camphoceanaldehydic acid melted at 195 to 196°.

When *i*-camphor aldehydo acid is heated with acetic anhydride in a sealed tube, the result is (*d* + *l*)-acetoxy-*β*-campholide; m. p. 97 to 98°, b. p. 155 to 156° (4 mm.). From *d*-camphoceane aldehydoacid there is obtained by this method *l*-acetoxy-*β*-campholide, m. p. 124 to 125°.



For the purpose of reduction, camphoceanaldehydic acid was dissolved in aqueous potassium carbonate and the solution reduced electrolytically in Bredt's reduction-apparatus[1]) with potassium amalgam as cathode. The (*d* + *l*)-*β*-campholide melted at 216 to 217°; the same melting point was observed with *d*-*β*-campholide prepared from *d*-camphoceanaldehydic acid by electrolytical reduction. Glacial acetic aced + hydrobromic acid dissolves the *β*-lactone without addition of hydrogen bromide.

Camphoceanaldehydic acid is sensitive towards the air, as was mentioned above. Even when the air is excluded an alteration takes place in the acid by deliquescing; from a determination of the molecular weight (by the cryoscopical method) of the liquefied *d*-acid, in benzene solution, it seemed to be a case of polymerization. The best way of keeping the aldehydo acid is to transform it into its stable acetate, acetoxy-*β*-campholide described above, which on saponification with sodium carbonate is easily retransformed into camphoceanaldehydic acid. *l*-Acetoxy-*β*-campholide metted at 124 to 125° the inactive isomeride at 97 to 98°. Bredt obtained a second isomeride of the acetates which points to stereoisomerism of the acetyl radicals comparable with the isomerism between borneol and *iso*borneol. Iso-*d*-acetoxy-*β*-campholid is formed on heating *d*-camphoceanaldehydic acid with an excess of acetic anhydride in a sealed tube to 100°. In addition to *d*-acetoxy-*β*-campholide, m. p. 126 to 128°, iso-*d*-acetoxy-*β*-campholide of m. p. 81 to 83° is the result. On saponification they yield both the same aldehydic acid. From (*d* + *l*)-camphoceanaldehydic acid equally two isomeric monoacetates obtained by prolonged beating with much acetic anhydride, in addition to the one described above (m. p. 97 to 98°) a different one of the m. p. 73 to 74°. Both the inactive acetates yield on saponification the same aldehydic acid.

At the conclusion of his paper, Bredt deals with a communication on intramolecular rearrangement of primary amines and amino acids in the camphoceane series and on the structure of *β*-campholide. He explains, on theoretical grounds, why the different authors found different properties of *β*-campholide.

Cinenic acid. — This acid, discovered years ago by Rupe[2]), exists in two isomeric forms known as *α*- and *β*-cinenic acid. Its constitution has been proved by synthesis performed by Rupe and Schlochoff[3]) and Rupe and Liechtenhan[4]) showing that the acid contains a hexacyclic ring consisting of five carbon atoms and one oxygen atom. In a communication on *α*- and *β*-cinenic acid, Rupe and Blechschmidt[5]) are of opinion that it is difficult to explain a *cis-trans*-isomerism on account of the alternating position of the methyl and the carboxyl groups with regard to the plane of the nucleus. A new possibility for explaining this isomerism has hitherto not been taken into consideration, *i. e.*, the assumption that cinenic acid might have the constitution of a hydroxylactone. Such a body might show the properties of an acid and would easily react, being an *ε*-lactone, with alkalies or even alkali carbonates. The body would then be the lactone of a dihydroxy acid (III) described by Rupe and Ronus[6]) as cinogenic acid, since on distillation water is split off, but with formation of *α*-cinenic acid and not of a lactone. Rupe and Blechschmidt, in their above-mentioned publication, have studied not only the method for preparing and purifying liquid *β*-cinenic acid, but also analyzed a number of salts of this acid as exactly as possible, the differences in the composition of the salts of a dihydroxy acid and an oxidic acid such as cinenic acid

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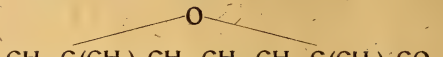
[1]) *Journ. f. prakt. Chem.* II. **84** (1911), 792; *Report* April **1912**, 191. — [2]) *Berichte* **33** (1900), 1129; *Report* October **1900**, 76. — [3]) *Ibidem* **38** (1905), 1498; *Report* October **1905**, 109. — [4]) *Ibidem* **41** (1908), 1278; *Report* October **1908**, 197. — [5]) *Journ. f. prakt. Chem.* II. **96** (1917), 59. — [6]) *Berichte* **34** (1901), 2193; *Report* October **1901**, 68.

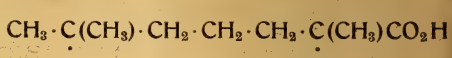
being sufficiently large to permit to decide with certainty whether it is a question or not of a hydroxylactone. Basing on their analyses the authors now are able to make good with certainty that the hydroxy lactone formula is impossible.

For preparing β-cinenic acid the finely powdered α-isomeride is boiled with sulphuric acid of 30 per cent.; already after one hour the solution, which in the beginning is clear, separates off oily drops of the new acid, of which the silver, magnesium, and calcium salts were prepared: —



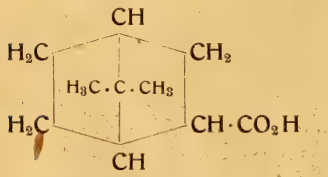
(I) α-Cinenic acid.

(II) Hydroxy lactone formula for cinenic acid.

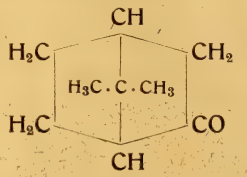


(III) Cinogenic acid.

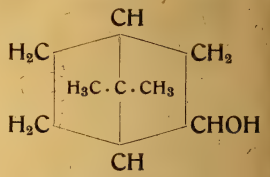
Fenchylanic acid. — Komppa and Hintikka[1]), when ozonizing α-fenchene, had obtained, in addition to α-fenchocamphorone, a monobasic saturated acid, fenchylanic acid, for which formula I could be established. The correctness of this formula has now been proved by G. Komppa and R. H. Roschier[2]) by total synthesis by means of rac.-α-fenchocamphorone (II). The latter was reduced by sodium and absolute alcohol to *(d + l)*-α-fenchocamphorol (III), m. p. 122 to 124°; b. p. 203°. The chloride obtained therefrom by action of phosphorus pentachloride yielded on treatment with magnesium and carbon dioxide in absolute ether *(d + l)*-α-fenchylanic acid (*allo*-apocamphanic acid) (I), m. p. 105°. The formation of this acid from α-fenchene shows that the decomposition of the ozonide passes off not only in the normal way by splitting up of a carbon linking, but also without loss of carbon.



(I) α-Fenchylanic acid.



(II) α-Fenchocamphorone.



(III) α-Fenchocamphorol.

Pulegenic acid. — Many years ago Wallach[3]) described the formation of pulegenic acid from pulegone dibromide with alcoholic alkali. This transformation passes off, as Wallach[4]) now communicates, more satisfactorily with aqueous alkali. For obtaining the dibromide from commercial pulegone he recommends brominating with a little less than the theoretical amount of bromine in glacial acetic acid solution, since the impurities in pulegone yield easily bromo-substituted products. Pulegone dibromide is shaken for one hour, at ordinary temperature, with aqueous potash, then for three hours at 100°; the unattacked pulegone and the methyl*cyclo*hexanone formed by hydrolysis are removed by steam distillation.

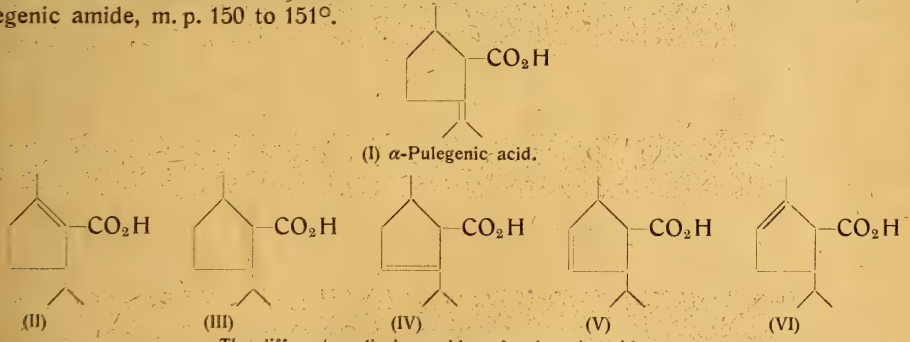
---

[1]) Comp. Komppa and Roschier, *Ann. Acad. Scient. Fennicæ, ser. A*, vol. X. **3** (1916), 3; *Chem. Zentralbl.* **1917**, I. 751; *Report* **1917**, 144. — [2]) *Ibidem* vol. X. **18** (1917), 1; *Chem. Zentralbl.* **1918**, I. 623. — [3]) *Liebig's Annalen* **289** (1895), 350; **300** (1898), 259; **327** (1903), 125; *Report* April **1896**, 44; October **1898**, 52; October **1903**, 90. — [4]) *Liebig's Annalen* **414** (1917), 234.

Of pulegenic acid, five isomerides must be able to exist according to the position of the double-linking within the nucleus: — Δ^1- (II), Δ^2- (III), Δ^3- (IV), Δ^4- (V), and Δ^5-methyl-*1-iso*propyl-*3-cyclo*pentene-*2*-carboxylic acid (VI). All of them must yield on addition of hydrogen, the identical saturated dihydro acid. The acid with semicyclic double-linking had formerly[1]) been found to be more difficult to reduce than were the isomerides with the double-bond in the nucleus, and that the acid amides add hydrogen easier than the free acids. However, the amide of pulegenic acid (I) is unsuitable for the preparation of the dihydropulegenic acid. It is far more advantageous to isomerize pulegenic acid by the method described formerly[2]) by first preparing hydrochloropulegenic methyl ester, then abstracting hydrogen chloride with simultaneous saponification, obtaining thereby a mixture of pulegenic acids. When this is distilled at ordinary pressure, the ordinary acid is decomposed with formation of pulegene and carbon dioxide, the isomeric modification, however, boiling with slight decomposition between 256 and 260°. The amide of this acid adds hydrogen easily, in presence of colloidal palladium, yielding thus dihydropulegenic amide[3]), m. p. 150 to 151° which can be hydrolyzed into the acid. A far more convenient method for preparing the free saturated acid is to abstract hydrogen chloride from hydrochloropulegenic ester by heating with an organic base and to reduce and then saponify the unsaturated ester. The free dihydropulegenic acid obtained from the ester boils at 139° (12 mm.). Eykman[4]), too, had arrived at this acid by reducing pulegenic acid with nickel and hydrogen.

On heating dihydropulegenic amide with bromine and alkali a base is formed, the acetyl derivate of which melted at 132°.

For obtaining pulegenic acid, also carvone may be used as primary material which is transformed, *viâ* dihydrocarvenolide, into hydrochloropulegenic ester. Wallach[5]), already years ago, had recognized the identity of *D,l*-dihydrocarvenolide with dihydropulegenolide. Dihydrocarvenolide is difficult to hydrolyze; better than with ordinary alcoholic potash it is split up with amylalcoholic potash into a hydroxy derivative of dihydrocarvenolic acid. On reducing the amide of this acid Wallach obtained dihydropulegenic amide, m. p. 150 to 151°.



(I) α-Pulegenic acid.

(II) (III) (IV) (V) (VI)

The different cyclic isomerides of pulegenic acid.

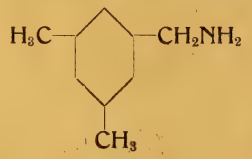
Nitrogenous Bodies.

The cyclylmethylamines $(CH_2)_x{>}CH{\cdot}CH_2{\cdot}NH_2$ show the tendency to yield when treated with nitrogen trioxide not only the corresponding alcohols, but also, with a

[1]) *Liebig's Annalen* **379** (1911), 213; **381** (1911), 78; **392** (1912), 57; *Report* April **1911**, 184; October **1911**, 126; April **1913**, 149. — [2]) *Ibidem* **296** (1897), 261. — [3]) Described in *Liebig's Annalen* **392** (1912), 58; *Report* April **1913**, 149. — [4]) *Chem. Zentralbl.* **1911**, II. 1030. — [5]) *Liebig's Annalen* **300** (1898), 262; **381** (1911), 69; **392** (1912), 49; *Report* October **1898**, 52; October **1911**, 126; April **1913**, 149.

strange molecular rearrangement, alcohols of higher molecular ring-systems[1]). Wallach[2]) now reports on experiments conducted with the purpose of investigating this reaction. The base obtained by reducing the oxime of hexahydro-*p*-acetyltoluene, yields after treatment with nitrous acid the corresponding secondary alcohol H_3C—⬡—$CH(OH)\cdot CH_3$.

1,5-Dimethyl*cyclo*hexenone-*3* was condensed with zinc and ethyl bromoacetate and the unsaturated acid (obtained in the familiar manner from the intermediate hydroxy ester) reduced according to Skita to the saturated *1,5*-dimethyl*cyclo*hexane-*3*-acetic acid. The amide of this saturated acid, when treated with bromine and alkali, yielded a base $C_9H_{17}\cdot NH_2$. The hydrochloride of this base, on treatment with sodium nitrite, gave rise to an oil which, on oxidation with chromic acid, yielded a body with the character of a cyclic ketone. Hence, one of the intramolecular transpositions characteristic of cyclylmethylamines when reacting with nitrous acid had here taken place.



Base $C_9H_{17}NH_2$.

[1]) Comp. Wallach, *Terpene und Campher*. 2nd ed., Leipzig **1914**, p. 154. — [2]) *Liebig's Annalen* **414** (1917), 229.

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SEMI-ANNUAL REPORT

on

Essential Oils,

Synthetic Perfumes, &c.

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List of abbreviations.

d = specific gravity.
$d_{20°}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d^{20°}_{4°}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
$n_{D20°}$ = index of refraction at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Scientific and other Notes on Essential Oils.

Ajowan Oil. The ajowan plant *(Ptychotis Ajowan,* D. C.; *Carum Ajowan,* Benth. et Hook.; *C. copticum,* Benth.; *Umbelliferæ),* hitherto grown exclusively in British India, has now been cultivated in the Seychelles and Montserrat by way of trial[1]). The seeds from the Seychelles looked sickly, but contained about 9 per cent. of oil, the thymol content of which was 38 per cent., whereas the Indian seeds yield only 3 to 4 per cent. of oil with a thymol content of 40 to 55 per cent. Although the Indian oil is richer in thymol, the seeds from the Seychelles offer an advantage owing to the higher percentage of oil. The seeds from Montserrat yielded 3,1 per cent. of oil, containing 54 per cent. of thymol; $d_{15^\circ}^{15^\circ}$ 0,935; $\alpha_D + 0{,}90^\circ$. The crop took place six months after sowing and amounted to 1128 lbs. per acre.

The Imperial Institute thinks this result is encouraging, but the distillation should be carried out on the spot.

As to ajowan oils from Montserrat and St. Kitts, see page 75 of this *Report.*

Almond Oil, bitter. In our previous *Report* (p. 5), we already pointed out the disgraceful conditions prevailing in the trade with bitter almond oil. Meanwhile, they have become still worse. Out of the uncommonly numerous samples of "genuine bitter almond oil, free from prussic acid", received by our analytical laboratory, there was not even a single one that stood the test! They all contained more or less chlorine and were therefore composed, entirely or in part, of common, crude benzaldehyde. It is a very great pity that even important firms take part in this cheating and have not the courage to acknowledge that, for the time being they neither have the genuine article in stock nor can procure it.

We would lay special stress upon the fact that true bitter almond oil never contains even the slightest trace of chlorine compounds and a great lack of knowledge is betrayed, if the seller asserts, as has been done in a case we know of, that chlorine reactions are not seldom with genuine oils. The "expert" in question even went so far as to declare a chlorine reaction possible, if the bottle has previously been rinsed with water. As we stated already many years ago (*Report* April 1891, 7, footnote) anorganic chlorides, as would come into consideration with ordinary water, cannot be detected at all through our combustion method, but exclusively organic chlorine compounds, the origin of which can not be doubted for an instant, if found in bitter almond oil.

We would refer, besides, to the notes on page 64 of this *Report,* regarding the presence of chlorine in benzaldehyde.

E. Bourquelot[2]) has published a short article on the nomenclature of the cyanogenous glucosides of the amygdaline group, in which he mentions that there are six

[1]) *Bull. Imp. Inst.* **16** (1918), 30; *Journ. Soc. chem. Industry* **37** (1918) A. 604. — [2]) *Journ. de Pharm. et Chim.* VII. **17** (1918), 359.

glucosides that in contact with emulsine yield d-glucose, benzaldehyde and prussic acid. Three are monoglucosides; the other three, diglucosides of the nitrile of phenylglycolic acid. They are: —

amygdaline, discovered in 1830 by Robiquet and Boutron Charlard, a diglucoside;
amygdonitrile glucoside, discovered in 1895 by E. Fischer, a monoglucoside;
*iso*amygdaline, discovered in 1904 by H. D. Dakin, a diglucoside;
sambunigrine, discovered in 1905 by Bourquelot and Danjou, a monoglucoside;
prulaurasine, discovered in 1905 by Hérissey, a monoglucoside;
d-amygdaline, discovered in 1909 by Walker, a diglucoside.

Amygdaline has been isolated from bitter almonds, sambunigrine from elder leaves, prulaurasine from cherry laurel leaves, and amygdonitrile glucoside from the leaves of *Prunus Padus*, L. Armstrong and Horton suggested calling this glucoside prunasine, the choice of which name does not meet with Bourquelot's approval, as more recent investigators classify the tree as belonging to to the *Cerasus* family and as *Prunus* species do not contain the glucoside.

Prunasine, prulaurasine and sambunigrine, when treated with concentrated hydrochloric acid and heated, yield ammonia, glucose and *l*-, *i*- or *d*-phenylglycolic acid, respectively. Amygdaline, thus treated, yields *l*-phenylglycolic acid and is therefore a glucoprunasine, *iso*amygdaline yields *i*-phenylglycolic acid and is therefore a glucoprulaurasine, and *d*-amygdaline yields *d*-phenylglycolic acid and is therefore a glucosambunigrine. On treating amygdaline, *iso*amygdaline and *d*-amygdaline with the ferment from dessiccated yeast, prunasine, prulaurasine and sambunigrine are formed, respectively.

All these glucosides have been discussed in previous *Reports*[1]).

Oil of Amorpha fruticosa. V. Pavesi[2]) obtained at the time an oil from the fruits of the legumen *Amorpha fruticosa*, L., but only described its properties, Y. Shinosaki and K. Hoshino[3]) now report on the constituents. They obtained about 1.1 per cent. of oil, the smell of which resembled pepper oil: $d_{15°}$ 0,9125; $\alpha_D \pm 0$; $n_{D20°}$ 1.5032; acid v. 0; sap. v. after acetylation 40.51; soluble in 10 vols. of alcohol 90 per cent. On fractionation, 0.5 per cent. boiled between 95 and 110°, 7.8 per cent. between 110 and 115°, 47.9 per cent. between 115 and 120°, 22.6 per cent. between 120 and 125°, 5.7 per cent. between 125 and 138°, at a pressure of 4 mm. The third and fourth fractions consisted in the main of cadinene and other sesquiterpenes, whereas the last fraction contained a considerable quantity of a sesquiterpene alcohol melting at about 118°. In addition, the oil contained small quantities of an aldehyde or a ketone, as the experimentors infer from the presence of a crystalline bisulphite compound.

It seems that the plant is called "Manchuria", in Japan.

The abstract does not give a clue as to how the several components were characterized.

Angelica Oil. We have repeatedly reported on the cultivation of angelica (*Archangelica officinalis*, Hoffm., *Umbelliferæ*)[4]). B. Pater[5]) describes a little more fully

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[1]) Comp. *e. g. Reports* October **1905**, 110; April **1906**, 105; April **1907**, 128; October **1907**, 11, 135; April **1908**, 12; October **1909**, 17; April/October **1918**, 5. — [2]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 611. — [3]) *J. Chem. Ind.*, Tokyo **21** (1918), 774; *Journ. Soc. chem. Industry* **38** (1919) A. 27; *Perfum. Record* **10** (1919) 89. — [4]) Comp. for instance *Report* October **1918**, 78. — [5]) Report on the trial fields for medicinal plants of Kolozsvár agricultural academy. No. 3, Kolozsvár 1918, p. 24. According to a reprint kindly sent us.

the conditions under which this aromatic plant is grown. He too lays stress upon the fact that it is of the utmost importance to use first class fresh seeds, because angelica seeds lose the faculty to germinate after a very short time[1]). Pater's publication does not contain any fresh information and the particulars given regarding the costs of production are only of local interest.

Oil of Sweet Basil. An oil of sweet basil obtained in the Seychelles[2]) (yield 0.21 per cent.) showed the following properties: $d_{15°}$ 0.962, $\alpha_{D28°} + 0.82°$, $n_{D21°}$ 1.514, acid v. 0.8, sap. v. 2.5, soluble with turbidity in 4 vols. of alcohol 80 per cent. Even in 10 vols. the solution is not clear. This oil seems to contain anethole and methylchavicole. It seems to be of little commercial interest.

Bay Oil. As is known, there exists a variety of the true bay-tree *(Pimenta acris,* Wight et Arnott, *Myrtaceæ:* West Indian Bay-tree, *"Bois d'Inde"),* smelling of lemon *(Pimenta acris* var. *citrifolia: "Bois d'Inde Citronelle")* and yielding an inferior oil. Another variety[3]) is known as *"Bois d'Inde Anis",* which likewise contains an inferior oil. As the leaves of these two varieties are often mixted with the genuine material, in Dominica, the oil obtained there is of less value. The distillers are greatly inconvenienced thereby and incur losses, as in the long run the renown of the Dominican Bay oil suffers from this state of affairs. Material from the three plants has been carefully examined at Kew, but it proved impossible to find any morphological criterion for a sure differentiation.

The occurrence of physiologically different forms, which however do not distinguish themselves at all morphologically, has been observed too with other aromatic plants, such as the camphor tree and certain *Cymbopogon* species.

Oil of Boswellia serrata. On a previous occasion, we discussed a publication[4]) on the oil of *Boswellia serrata,* with which experiments had been made in the Forest Research Institute at Dehra Dun. The following later notice[5]) emanates apparently from the same source. The above named Indian Institute carried out investigations with regard to the manufacture of turpentine oil, resin and gum from *Boswellia serrata,* a tree occurring in great abundance in the district of Kandesh, but which grows frequently also in other parts of the country. The yield in gum resin depends upon the age of the trees and the way of tapping them. Trees of 30 inches in circumference yield between 1½ to 2¼ lbs. in the tapping period (December to July). The costs of production amount to 1 d or ½ d per lb.; in some districts they are still smaller. On an average, the gum resin yields 8 to 9 per cent. essential oil, 55 to 57 per cent. rosin and 20 to 23 per cent. gum. The technical separation of these three bodies can be carried out without any great loss of material and might be developed into a new, important branch of Indian industry. The oil above mentioned (pinene) resembles the best American and French turpentine oils. It could therefore enter into successful competition with the former, all the more so as its drying capacity is even greater, though it does not impart to the varnish the same lustre. The rosin would be a good substitute for American rosin and is fit for being used in varnishes. As to the gum, it is true that it is somewhat inferior to the commercial quality, but would do quite well for

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[1]) Comp. Pater, *Pharm. Post* **1916**; *Reports* October **1917**, 110, October **1918**, 101. — [2]) *Bull. Imp. Inst.* **16** (1918), 32; *Journ. Soc. chem. Industry* **37** (1918), A. 604. — [3]) *Kew Bulletin; Chemist and Druggist* **90** (1918), 728. — [4]) *Bull. Imp. Inst.* **13** (1915), 351; *Report* October **1916**, 6. — [5]) *Die Seife* **3** (1919), 890.

dressing textiles. English and Indian manufacturers, who had been asked to try the three products, have reported favourably as to their industrial use.

Buchu leaf Oil. On page 33 of our *April Report* **1914**, we mentioned a publication of van Wielligh[1]) on the occurrence of the buchu plant in South Africa, that had been discussed already in the *"Chemist and Druggist"*. The treatise has now been discussed more fully elsewhere[2]) and as a keener interest than before seems to be shown for buchu leaves[3]) we should like to make our readers better acquainted with the matter.

Three species are in medicinal use; *viz.*:—

1. *Barosma serratifolia* (*"Kloof"* buchu). It grows on a somewhat damp soil, reaches a height of 4 feet on an average, sometimes even 10 feet, and occurs in gorges, 500 to 1000 feet above the sea level, between shrubs and granite *débris*, in the shade of trees. Black, sandy clay containing a considerable proportion of decayed vegetable matter, is reported to be specially favourable for its growth.

2. *Barosma betulina* (Mountain buchu) is probably the most valuable kind. It is more compact and smaller than *B. serratifolia*, reaches 3 to 4 feet in height and is found frequently on slopes about 1000 to 2000 feet above sea level. Red, sandy clay or red sandstone and quartzite seem to foster its growth.

3. *Barosma crenulata* is not so widely spread and less known, in consequence.

The buchu shrub is not satisfied with every kind of soil. Its natural habitat is neither on calcareous, nor on saliferous, sandy or heavy clayey soil. It is said that the cultivation succeeds best on sandy, well-drained and deeply ploughed clay, which is not watered by salt rivers.

The buchu plant can be propagated through seeds and slips. The seeds are generally sown before the cold season, in seed frames or on beds. The former are mostly filled with a mixture of equal parts of mould and sand, placed on a shady, warm spot and kept damp. The seeds, which ought to lie 1¼ cm. under the surface, germinate after some weeks, after which the frames can be exposed to the morning sun. Afterwards, only a protection against frost and sharp wind is necessary and the soil must be kept moderatly damp, but absolutely free from weeds.

If the seeds are sown on beds, these must be dug over very deeply, the soil being partly replaced by mould and sandy clay. They are often covered with branches, as too much sunshine is harmful at first. As soon as the young plants appear, the beds can have a little more sunshine, so long as it is not too glaring.

Transplanting generally takes place when the air is not too dry. The soil is ploughed about 2 feet deep and, as a rule, the distance between the plants is 5 feet. Afterwards, the beds need only be hoed and kept damp. When hoeing, it must be taken into consideration that the roots do not cling so much to the soil as is the case with other shrubs.

Cade Oil. It is generally classified among the essential oils, although it is obtained from the wood of the conifer *Juniperus Oxycedrus*, L., through a kind of dry distillation, which we described occasionally in our *Reports*[4]). In a recent publication, H. Huerre[5]) reports on the essential oil contained in the wood of *Juniperus*

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[1]) *Agricultural Journal of the Union of South Africa*, Juli 113. — [2]) Commerce Reports of June 11th 1918; *Americ. Journ. Pharm.* **90** (1918), 600. — [3]) Comp. *Report* April/October **1918**, 10. — [4]) Comp. *Reports* October **1906**, 13, April **1907**, 14; October **1908**, 24; April **1909**, 58. — [5]) *Journ. de Pharm. et Chim.* VII. **12** (1915), 273; *Report* October **1916**, 33.

Oxycedrus. In order to find out what becomes of this oil when cade oil is prepared, he[1]) subjected to a comparative investigation the products which, on the one hand, were obtained on dry distillation from the wood of *Juniperus Oxycedrus*, on the other hand resulted after previous removal of the essential oil. On direct distillation, 1 kilo of wood yielded on an average 81.11 grams of true cade oil, whereas only 56.26 grams of distillate were obtained from wood deprived of its essential oil. The difference corresponds to the oil content of the wood. Hirschsohn and Adam's reactions do not permit of differentiating between the two distillates. When shaken with 5 per cent. soda lye, the normal true cade oil gives of 5 per cent. of phenole-like constituents; the product obtained from wood deprived of its essential oil, about 10 per cent. Huerre found, that fractionated distillation is a good method of characterizing the genuine cade oil, but that the differences do not suffice to decide, whether wood deprived of its essential oil has been used. The saponification values for the oils freed from the phenols are 78 and 89, respectively. This difference is partly explained by the low saponification value of the essential oil contained in the normal product. In any case, the saponification value might serve as a criterion for the purity of the cade oil. It indicates that, in addition to phenol-like constituents, cade oil contains a considerable proportion of esters.

The wood of *Juniperus virginiana*, treated in the same way as *J. Oxycedrus*, yields 68 grams of oil per kilo, in addition to water, tar and a brilliant black residue. The oil, called virginol, smells strongly of pyroligneous acid, is lighter than water and more liquid than cade oil. 5 per cent. soda lye deprives it of 3.8 per cent. of phenols.

Dry distillation of the wood of the Lebanon cedar yielded on an average 75 grams of libanol[2]) per kilo, an oil smelling of pyroligneous acid, lighter than water, more mobile than cade oil and containing 9 per cent. of constituents soluble in alkali.

Cajuput Oil. In H. C. Schmid's[3]) article, discussed on page 80 of this *Report*, there are various interesting communications regarding cajuput oil and the cajuput tree. It occurs all over the island of Buru, but least on the rocky southern part. Where it thrives, only alang-alang grass[4]) can grow, all the other plants die. The Halifur, *i. e.* the native of Buru shifts his garden, as soon as a cajuput tree shows itself in the neighbourhood. He does not even try to destroy it.

The tree is most tenaceous of life and cannot even be extirpated through felling or burning down. If the alang-alang grass is burnt repeatedly, many bajuput trees and shrubs die down, it is true, but they sprout again afterwards.

As distinction is made between *Kajoepoetih merah* with red and *K. poetih* with white wood.

In Buru, the oil is distilled from the leaves of shrubs from six months old and upwards and only when this material is exhausted are the leaves of the *trees* used.

As soon as the cajuput shrubs in the neighbourhood are used up, the *"ketel"*[5]) has lost its value; however, this does not happen very soon, as the shrubs grow thickly.

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[1]) *Journ. de Pharm. et Chim.* VII. **19** (1919), 33, 65; *Chem. Zentralbl.* **1919**, II. 789. — [2]) The name of libanol is used already for the distillate obtained by steam from the Atlas cedar, *Cedrus atlantica*, Man. Comp. *Report* April **1902**, 12. — [3]) *Teysmannia* **25** (1914) 33. The author was at the time Civil Governor of Buru. — [4]) Alang-alang grass *(Imperata arundinácea*, Cyrill., var. *Koenigii*, Benth.; *Gramineæ)* is from 1 to 2 m. high and develops luxuriantly at once wherever the forest is cleared. It is a plague for agriculture, as its extirpation is extremely difficult. It seems to disappear in gardens, where pine-apples are grown, or near *Lantana Camara*. — [5]) See page 80, foot-note 5.

The distilling apparatus (the article contains some good views of the same and of cajuput trees) is very simple. It consists of a large, round cast iron basin *("Kwali")*, in which there stands a barrel, open at the bottom, for receiving the material to be distilled. The staves of the barrel are fastened with rattan rings and the joints made tight with cajuput bark. A wooden ring on the top of the barrel carries a tin head-piece with a copper helmet. The vapours are conducted through a zinc or copper tube into the refrigerator and the condensate passed through a funnel into gin bottles. Just above the bottom of the bottles, a hole of about 7 mm. in diameter has been made, and they are placed in a vessel nearly as high as themselves. The cajuput leaves are stamped into the barrel mentioned before, so that they form a firm mass. Then water is poured on and, if an adulteration is intended, petroleum. The whole arrangement stands on a hearth of fire-proof clay.

If the *"Ketel"* is situated near a river, the water in the refrigerator is renewed by a so-called *"Pantjoran"* (jet of water), but if water is scarce, it is only renewed for every fresh charge, which of course causes a loss of oil.

In the vessel containing the receiving bottle, the water, in the beginning stands only a little higher than the hole in the bottle. During the distillation, the water rises slowly inside and outside the bottle. It is then allowed to flow over until the bottle is almost filled with oil. If there is enough water for refrigeration, 2 to 4 1/2 bottles of oil can be distilled in a *"Ketel"* within 24 hours; if water is scarce, only 1 to 1 1/2 bottles. A bottle contains about 1 1/2 litre.

The oil is then taken to the forestallers, who fill it into *"Tempajans"* (by earthenware jars). The green colour is often intensified by throwing copper coins into the oil. A certain firm has also supplied the dealers with a substance — according to the author perhaps a copper salt — for the same purpuse.

From the *"Tempajans"*, the oil is filled in bottles, mostly beer bottles, which are corked and covered with sealing wax. Then the product is ready for transport. The petroleum is very likely often added to the oil in the *"Tempajans"*.

It has been reported that urine was added sometimes, in order to raise the specific gravity, which is lessened by the petroleum. But as urine does not mix with the oil, the author thinks — as we do — that this is a fable.

The boxes used for packing are made of gaba-gaba (dried leaf-stalks of the sago-palm), joined together with bamboo nails[1]). Such a box contains 25 bottles. The spaces in between are filled up with dried "Ampas" (refuse) of cajuput leaves. Another excellent packing material is the cajuput bark, of which large pieces can be taken from the tree without doing it any harm.

Camphor Oil. According to a notice in *The Board of Trade Journal* of 6. VI. 1918[2]) the weather was very unfavourable in Formosa in 1917. As the production of camphor did not pay, in comparison with other work, such as burning charcoal, the output of the fiscal year 1718/18 did not come up to the expectations. In the period from 1. IV. 1917 to 31. III. 1918, it amounted to about 60000 piculs[3]), as compared with 89.300 piculs in 1916/17, whereas the corresponding figures for Japan were 20000 and 39600 piculs, respectively. In consequence, the totals for both producing countries together were 80000 piculs in 1917/18 and 128900 piculs in 1916/17.

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[1]) Depicted in Tschirch, *Indische Heil- und Nutzpflanzen* (Indian medicinal and otherwise useful Plants), Berlin 1892, plate 75. — [2]) *Nachr. f. Hand., Ind. u. Landw.* **1918**, no. 93, p. 6. — [3]) 1 picul = 60.453 kos.

The following tables show the exports of crude camphor from Formosa and of refined camphor from Japan in 1916 and 1917:—

Exports to	Refined Camphor from Japan		Crude camphor from Formosa	
	1916 kin	1917 kin	1916 kin	1917 kin
Great Britain	639 125	145 130	838 500	761 800
British-India	1 416 041	1 082 490	—	—
Australia	92 605	112 400	—	—
France	379 862	66 618	270 200	76 500
United States	2 654 438	1 493 135	4 680 759	4 065 600
Japan	—	—	2 002 045	1 252 272
Asiatic-Russia	447 068	65 446	75 000	—
China	—	—	14	89
Other countries	124 713	154 696	—	—
Total	5 753 852	3 119 915	7 866 509	6 156 261

According to another source the exports of camphor from Japan during the first half of the last three years came up to[1]):—

	1917 kin	1918 kin	1919 kin	
British-India	412 447	277 511	25 303	
Great Britain	46 583	292 443	50 123	
France	15 165	23 965	48 813	
United States	1 156 838	383 073	920 447	
Australia	17 392	62 907	1 633	
Other countries	76 801	118 634	44 665	
	1 725 226	1 158 533	1 090 984	kin
to the value of	2 889 756	2 306 704	3 012 571	Yen

The exports of camphor oil during the same period were:—

	1917	1918	1919
kin	920 660	539 623	266 439
to the value of Yen	168 268	108 069	66 244

Formosa's camphor production decreased considerably[2]) in 1918, owing to the fact that the workers obtained better wages in other industries. In 1917/18, Formosa produced 60 000 piculs of crude camphor, against 89 000 piculs in the previous year. As the native camphor refineries and celluloid factories demanded 72 000 piculs, only 8000 piculs would have remained for export(?), whereas in reality double this quantity was sent abroad. The dealers were obliged to refuse orders and there was a scarcity in the country itself. The prices were from Yen 2.10 to 2.40 per lb. During the first six months of 1918, the exports totalled 1 422 222 kin, to the value of 2.9 million Yen, distributed as follows:—

317 000 kin to British-India, 474 000 kin to the United States,
345 000 „ „ Great Britain, 85 000 „ „ Australia,
31 000 „ „ France, 170 000 „ „ other countries.

[1]) *Chemist and Druggist* **91** (1919), 915. — [2]) *Chemical Tr. Journ.*, 15. 6.; *Japan Advertiser*, 29. 6.; *Oil and Colour Tr. Journ.*, 14. 12. 18; *Japan Chron.*, 9. 1. 19.

As the camphor refineries complain of being insufficiently provided with crude camphor by the Monopoly Bureau, leading firms like Suzuki, Akashi and others have tried to unite a number of small Formosa concerns producing crude camphor to form a big company. It was to be founded this spring with a capital of 6 million Yen with the aim of increasing the production of crude camphor.

The Formosa Camphor Refining Company, which started to work in November 1917, will require most likely 10000 piculs, whereas the new combine of camphor refining works in Kobe, founded on 5th February and known under the name of Nippon Camphor Refining Company, will consume 50000 piculs yearly. Besides, 12000 piculs annually must be handed over to the celluloid factories, so that the total consumption of crude camphor in Japan amounts to 72000 piculs per year. If the production does not exceed 80000 piculs, only 8000 piculs will be available for export. On the other hand, the output in 1916 was 128900 piculs, which shows that in good years the export is considerably larger. However, prospects for an increase of the camphor production are not favourable just now, a further decrease being more likely. The hope, nourished in Japan a few years ago, that camphor might be obtained from the leaves of the tree, has not been realized, and the yield from young trees has not sufficed. The roots of the old trees have already been dug up and used, and every available source has been taken advantage of. Working in the remoter woods in still difficult and dangerous, because of the savages, and the gain would not correspond to the danger.

The Government General of Formosa has recently raised the workers' wages by 3 Yen for 100 kin of camphor and 1.50 Yen for the oil, but even this has not had the desired effect.

The New York Journal of Commerce of 27. VIII. 1918[1]) reports that the Japanese Government appointed a committee of seven officials and experts in order to watch the production of camphor and the market conditions. The committee is intended to prevent the decay of the camphor industry, which is to be feared in consequence of the probable decrease of the production in 1918 by 1000000 lbs.

According to *The Chemical Trade Journal*[2]) the camphor production in Japan and Formosa, in the fiscal year ending on 31. 3. 1918, came up to 10678800 lbs., of which the Monopoly Bureau bought 10362000 lbs., *i. e.* a decrease of 4989600 lbs. in comparison with the previous fiscal year. The Monopoly Bureau was unable to satisfy all the numerous demands from Europe and America, owing to the increasing home consumption. The 10362000 lbs. acquired by the Monopoly Bureau were disposed of as follows: 4276800 lbs. to the camphor works, 831600 lbs. to the celluloid factories, 343200 lbs. to the open market. The remaining 4910400 lbs, were exported. The public authorities promote the export of finished goods and hinder that of camphor.

Another periodical[3]) estimates the camphor output in Formosa at 5.3 million kin on an average for the last years, 3.5 million kin thereof being exported to England, France and America, up to 1916. Later on the export decreased in consequence of the high freights, whereas on the other hand the home demand for the manufacture of toys, buttons and other celluloid goods rose considerably. Since 1917, two thirds of the whole output are consumed in the country. For the current year, a decline of 14 per cent. is expected, owing to the epidemic of influenza and the fact that many workmen have gone over to other industries.

As per *The Board of Trade Journal* of 20. VI. 1918[4]), the camphor production in China has gone down very much. It was to be feared that in the near future China

[1]) *Nachr. f. Hand., Ind. u. Landw.* **1918**, no. 164, p. 5. — [2]) *Journ. Ind. Engin. Chemistry* **10** (1918), 1022. — [3]) The Japan Chronicle of 13. III.; *Nachr. f. Hand., Ind. u. Landw.* **1919**, n. 98, p. 6. — [4]) *Nachr. f. Hand., Ind. u. Landw.* **1918**, no. 99, p. 4.

might be unable to do much for covering the world's requirements. The state of affairs was to be deducted from the following extract of the *Encyclopædia Sinica:* In 1891, nearly 17 000 piculs were exported and the industry promised a good development. Then Formosa was resigned to Japan and the trade passed over into the hands of the Japanese. The world's requirements of camphor are covered almost entirly by Formosa, but with the aid of the Government, China could doubtlessly produce a large quantity of camphor. After Formosa had been relinquished, the province of Fukien was searched for camphor, as there are many camphor-trees in several prefectures. An official from Formosa obtained the monopoly of camphor production there and spread the knowledge of this industry. High profits soon led to exhaustive exploitation of the camphor forests. In 1906, there were 20 camphor distilleries going in Foochow, 11 000 piculs being exported. But soon all the accessible trees were felled, so that the industry may be considered as having ceased to exist in Fukien. Efforts have been made to develop it in Kiangsi, where camphor forests are found in the Kantschou and Kiangsi districts. In 1904, a factory was put to work in Kiukiang, the output of which now is 1600 piculs on an average. In South-Hupei, a syndicate owns the monopoly of camphor production. In 1903, a company was granted the privilege of producing the Tshekiang camphor, which occurs in Tshu-tshou. A small trade has started in consequence in Kiangsi. As per the Customs' report of 1900, there are numerous camphor-trees in South-West Yünnan and the Shan states. They wait so to speak for the industry and especially for favourable forwarding conditions. If the Government would support the industry, it could soon be revived and greatly extended. In 1916, the camphor exports totalled 2377 piculs to the value of 181 673 Taels, of which 1686 piculs went to Hongkong, 537 to the United States and 100 to British India.

As regards Formosa's production of camphor oil, which was absorbed almost entirely by Japan, it diminished, in 1917, from 6681673 to 5270533 lbs.[1]) The causes were shortage of hands and devastations by the natives as well as through hurricanes. Besides, it is reported from Japan that the stocks of camphor are very limited and that the celluloid factories had to close in part. The maximum price is 120 Yen per 100 kin, whereas 160 Yen are paid willingly in the open market. The demand has increased considerably everywhere.

The same periodical reports on the management of forests in Formosa. As the alleys and woods of *Cryptomeriæ,* cedars and other trees in the whole country testify, the Japanese people have always loved trees. This has induced them to plant woods in Formosa, especially of camphor-trees which are subject to a Government monopoly. The seeds are generally brought from Japan, as it is difficult to procure them on the spot, owing to the thick undergrowth. The trees are planted in isolated groups, all the surrounding shrubs and trees being burnt down beforehand. Next to the camphor-tree, the cypress *(Hinoki)* is the most valuable tree. It is likewise imported from Japan. All endeavours to distil oil from it, have failed, however. Trees yielding hard wood were also planted, but this was discontinued, owing to the difficulties of exporting the wood for lack of tonnage. Where there were considerable plantations, the trees were felled and used as fuel, the ground then being used for sugar-cane growing.

According to various papers[2]), the first plantation of camphor-trees in the United States (in Florida) yielded 10000 lbs. of crude camphor, last year. It covered 25 ha. Another paper[3]) declares the prospects of this industry to be fairly favourable. It reports

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[1]) *Der Neue Orient* **4** (1918), 39. — [2]) *Nieuwe Courant.* — *Züricher Post* of 15. VII, 18; *Chem. Industrie* **14** (1918) 189, 223. — [3]) *Perfum. Record* **10** (1919), 30.

of a grower, who produces 40 tons of camphor yearly. Compared with the world's consumption, this is very little, of course. In order to cover this, Florida would have to cultivate another 175000 acres of camphor-trees, the yield being about 20 tons per acre, and it takes five years before there is any.

For those interested in Florida's cultivation of camphor-trees, a treatise by F. A. Gudger[1]) is worth reading. As there is nothing essentially new in it and we have discussed the subject repeatedly in our *Reports*, we refrain from going into details[2]).

An English periodical[3]) has published an article on camphor oil and the possibility of extending the cultivation of camphor-trees in the British Empire. It is justly pointed out that there certainly are varieties of the common camphor-tree, the oil of which contains little or no camphor and shows other abnormal properties[4]), a fact that ought to be taken into consideration when planting. It would be necessary to establish through scientific investigation which varieties produce the valuable oils and under what conditons. It would likewise be important to know which variety yields the oil richest in safrole. Possibly, the elevation above the level of the sea, the surroundings, the soil and other circumstances, insufficiently observed so far, might influence the quality of the oil.

The article also contains communications concerning the cultivation of the camphor-tree, but nothing really new.

Cananga Oil. As to the cultivation of the cananga-tree in the Dutch Indies, see page 82 of this *Report*.

Caraway Oil. According to a notice from the Dutch Ministery of Agriculture of July 19th, there were only 609 ha. planted with caraway, this year, against 1666 ha. in 1918. The exports are said to be greatly handicapped by the high prices which the committee for foreign trade exacts. In consequence, about 150000 bags are supposed to be unsold, the total quantity available at the beginning of the new crop being estimated at 200000 bags minumum. No wonder that the farmers are not very keen on caraway growing, this year, especially as prices have gone down from fl. 44.50. (before the war fl. 15.—!) to fl. 30.—. per 50 kos. Some farmers are even ready to contract for delivery in August 1920 at the rate of fl. 25.50.

In Germany, caraway growing has been made more attractive in various parts by the high prices paid for spices during the war. Fairly considerable quantities of good quality were offered from East Prussia, the Province of Saxony and Sleswig-Holstein and readily sold in view of the unfavourable rates of exchange which are almost prohibitive for the import from Holland. It remains to be seen whether caraway growing on a large scale can be successfully continued in Germany.

Owing to the scarcity of caraway seeds, the fruits of *Peucedanum Sowa* (*Anethum Sowa*, Roxb.; *Peucedanum graveolens*, Benth. et Hook., umbelliferæ), known as Indian dill and the taste of which recalls that of caraway, have been sold in England and France as a substitute[5]). Besides, another kind of caraway has been offered on the London market. It came from Tunis and had a similar aroma to that of Dutch or English caraway. The article does not mention the botanical origin of this substitute, which may come from a local variety of the ordinary caraway plant.

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[1]) *Du Pont Magazine; Perfum. Record* **10** (1919), 8. — [2]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 447. — [3]) *Perfum. Record* **10** (1919), 57. — [4]) Comp. for instance *Report* October **1918**, 14. — [5]) *Chemist and Druggist* **90** (1918), 796.

A caraway oil offered to us from Hamburg was conspicuous by its abnormal constants, being far too heavy, specially well soluble and of too small a rotatory power: $d_{15°}$ 1.0342, α_D +35°10', soluble in about 1 vol. and more alcohol of 80 per cent. As there was no agreement with either caraway oil or carvone, it was natural to look out for an adulteration. The examination revealed that, in opposition to caraway oil, the stuff contained a considerable proportion of ester, which resembled very much the phthalic ester used in perfumery. The acid isolated from the saponification lye was then recognized as phthalic acid, melting at about 196°. The ester value determined (325.8), corresponded to an ester content of 56.4 per cent., calculated as dimethyl phthalate.

This case shows that caution is required even in buying oils which, such as caraway oil, are very seldom faked.

Cassia Oil. As per a communication of the American Consulate General at Hongkong[1]) the exports of cassia oil have decreased considerably, in 1918, the shipments to Europe having gone down by two thirds. The declared export of cassia oil to the United States, in 1918, amounted to 139938 lbs. to the value of $ 124465.—, as compared with 112003 lbs. to the value of $ 124503.—, in 1917.

The adulteration with phthalester has, of late, not been restricted only to the oils estimated according to their ester content, when the purpose is to make the ester content appear as high as possible, but is now in use with almost any oil. As in these other cases the original aim does not enter into consideration, the addition is no longer so modest as before, but reaches an astounding proportion. First in the ranks is a little Leipzig firm, scarcely known before the war, but who through this bad, though certainly very remunerative, practice has attained to such a shameful notoriety, that we have had to stigmatize them repeatedly in this *Report*. Among the oils "transformed" by them is a cassia oil, submitted to us from Hamburg for inspection. It betrayed at once its having been faked by its excessively high specific gravity ($d_{15°}$ 1.1108) and above all by the altogether insufficient aldehyde content (about 15 per cent.). The saponification showed how this had been done. Whereas cassia oil contains scarcely any saponifiable components, the sample showed an ester value of 390.5. The acid separated from the lye was recognized by its m.p. (195 to 197°) as phthalic acid. It yielded, besides, a sublimate in the form of fine needles, melting at 130° and identical with phthalic acid anhydride. The adulterant was thus proved to be phthalic ester, the quantity added amounting to about 67 per cent., calculated as dimethyl phthalate.

F. D. Dodge[2]) has continued his investigations of cassia oil, discussed by us[3]) at the time, and discovered again some new constituents.

He examined two oils, the one of which (A), obtained by him through rectifying a pure commercial oil, showed the following properties: $d_{25°}$ 1.0528, α_D feebly to the right, aldehyde content 88 per cent. The other oil (B) answered the requirements of the U. S. P.: $d_{25°}$ 1.0514, α_D feebly to the right, aldehyde content 80 per cent. Both oils were free from rosin.

He shook 1 lb. of each with about 5 lbs. of sodium bisulphite solution, removed the non-aldehydes and heated the solution on a water-bath until the transformation into the sulphonate was complete. After cooling down, sodium carbonate was added to the whole liquid until it had become strongly alkaline, when he extracted it with

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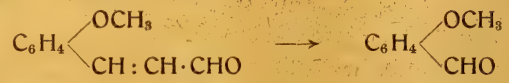
[1]) *Handelsberichten (Den Haag)* **13** (1919), 362. — [2]) *Journ. Ind. and Engin. Chemistry* **10** (1918), 1005. — [3]) *Report* October **1916**, 12.

ether and removed the salicyladehyde from the ethereal solution by means of normal soda lye, the other aldehydes with strong bisulphite lye. From the alkaline solution, he obtained the salicylaldehyde through acidulation and extraction with ether; the other aldehydes, from bisulphite solution by neutralization and shaking with ether. In this manner, he found the following composition: —

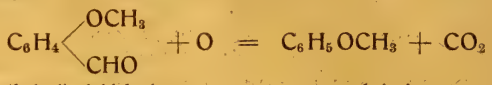
	A	B
original	453 grs.	453 grs.
non-aldehydes	about 50 grs.	about 80 grs.
salicylaldehyde	0,985 grs.	1,110 grs.
other aldehydes	3,850 grs.	4,860 grs.
cinnamaldehyde	not recovered.	

The aldehydes recovered smelled strongly of benzaldehyde. They dissolved in bisulphite solution, evolving heat, but depositing very little crystalline matter. On remaining in contact with the air, an acid formed (m.p. 91 to 93°), which proved to be impure benzoic acid. The oxidation of the aldehydes with potassium permanganate led to benzoic acid, which might point to hydrocinnamaldehyde. Dodge, in consequence, oxidized 3 grs. of the mixture of aldehydes with 30 cc. of official hydrogen peroxide in the presence of a few drops of ferrichloride solution, keeping the solution slightly alkaline by means of soda lye. A smell of anisole was to be noticed during the process, but no hydrocinnamic acid was to be detected. On oximation, the mixture of aldehydes yielded an oxime melting at 90°, which might be identical with hydrocinnamaldoxime (m.p. 93 to 94°) or methylsalicylaldoxime (m.p. 92°). Dodge is of opinion that the presence of methylsalicylaldehyde could be explained by the oxidation of the methyl-cumaraldehyde present in cassia oil: —



Methylcumaraldehyde. Methylsalicylaldehyde.

Methylsalicylaldehyde can be further oxidized to form anisole: —



Methylsalicylaldehyde. Anisole.

In order to characterize the oxime still better, Dodge transformed it into methyl-salicylic acid through oxidation with potassium permanganate, after the conversion of the oxime in the nitrile and the saponification of the latter had failed to yield an acid of a determined melting point.

The oxidation with permanganate, in his opinion a new method of converting an oxime into the corresponding acid, seems to be applicable if the acid obtained sufficiently resists the action of the potassium permanganate.

He mixed the solution of 0.231 gram of oxime in a few drops of methyl alcohol with 2 cc. N/2 potash lye and added little by little sufficient of a 5 per cent. potassium permanganate solution until there was no further oxidation, when he acidulated with sulphuric acid and shook with ether. The acid thus obtained being still impure, owing to an oily admixture, he repeated the oxidation with potassium permanganate, did not extract with ether, however, but allowed the acidulated liquid to stand. An acid then deposited, melting at 89°, which proved to be methyl salicylic acid.

On further treatment of the non-aldehyde constituents of the oil A, a small quantity of a petroleum fraction was discovered, originating most likely from an adulteration of the oil.

Champaca Oil. As to the cultivation of the champaca-tree in the Dutch Indies, see p. 82 of this *Report*.

Cherry-laurel Oil. On page 13 of our *Report* of October **1917**, a treatise by O. Rössler[1]) on cherry-laurel water has been discussed. In continuation thereof, R. Holdermann[2]) reports on the fluctuations in strength of the product, which he determined according to the observations made by Unnay in 1869.

Leaves of the same tree were used for the experiments in either case. From 1 ko. of leaves, 1 ko. of distillate was prepared in the manner described in the article, the results being as follows: —

		total hydrocyanic ‰	free acid ‰	proportion of free acid in the total hydrocyanic acid.
1917	June	1.055	0.162	1:6.5
1917	July after a rainy period	0.833	0.138	1:6.0
1917	August	1.08	0.193	1:5.6
1917	September	0.90	0.16	1:5.6
1917	October	0.492	—	—
1918	April	0.664	0.166	1:4

In April 1918, leaves from the previous year were used which had remained on the tree. In agreement with Unnay's indications, it resulted that the old leaves in autumn or spring yield considerably less hydrocyanic acid than the young ones during the summer months. The proportion of free acid in the total contents decreases with the age of the leaves. Leaves distilled between June and September always yield a product answering the requirements of the pharmacopœia. In order to secure the prescribed content, it is necessary to collect first $\frac{3}{4}$ ko. of the strong first running and to adjust with the weaker second running.

The crushed fruits yield a very aromatic distillate with only 0.243 ‰ of hydrocyanic acid.

As regards the preparation of benzaldehydehydrocyanide, used for ajusting weak distillates, it succeeds best as follows: —

Hydrocyanic acid is developed in the usual way from a mixture of potassium ferro(ferri-)cyanide and sulphuric acid and distilled into a receiver containing dilute alcohol. A corresponding quantity of benzaldehyde is added, after which there is no clear solution, part of the benzaldehyde depositing. After 3 days, however, the solution is clear. In one experiment the proportion of free acid in the total quantity was found to be 1:4.4. After 4 weeks, it was 1:6, the same as in natural cherry-laurel water. A dilution thereof with the prescribed proportion of alcohol and containing 1 ‰ of hydrocyanic acid was completely clear and colourless and answered the requirements of the pharmacopœia.

Cinnamon Oil, Ceylon. Ceylon's exports of cinnamon oil[3]) in 1917 were 78438 ozs., valued at 39928 rupees, compared with 10129 ozs., valued at 5857 rupees, in the year 1914. It was principally sent to the Straits Settlements, the United States and France, as is shown by the following figures: —

	1914 ozs.	1914 Rupees	1917 ozs.	1917 Rupees
Straits Settlements	7546	3620	35028	2050
United States	1500	1100	30660	17580
France	—	—	10350	17600
Great Britain	1083	1137	800	150

[1]) *Arch. der Pharm.* **255** (1917), 151. — [2]) *Ibidem* **257** (1919), 69. — [3]) *Perfum. Record* **9** (1918), 304.

The total exports of cinnamon leaf oil amounted to 95091 ozs., value 17996 rupees, in 1917, compared with 36936 ozs., valued at 3420 rupees, in 1914, of which the United Kingdom took 61568 ozs., value 13800 rupees, in 1917, and the total in 1914.

Two cinnamon oils, sent us for inspection, showed that phthalic ester had been used as an adulterant, one of the samples containing as much as two-thirds of it. In consequence the content of aldehydes was very low (about 20 per cent.) and, besides, these aldehydes were mostly benzaldehyde, whereas the presence of cinnamaldehyde was altogether uncertain. Under the circumstances, one cannot speak of an adulteration, but of an artificial mixture which can never serve as a substitute for cinnamon oil.

The other sample seemed to be similar, but the quantity at our diposal was so small that we could just prove the presence of the phthalic ester there not being enough oil left for determining the aldehydes.

On distilling a sample of cinnamon bark from the Gold Coast the Imperial Institute laboratories[1]) obtained 1.18 per cent. of a heavy oil, which separated from the aqueous distillate, and 0,3 per cent. of light oil, extracted from the distillate with ether. The odour of the heavy oil is very fragrant: $d\frac{15°}{15°}$ 1.042, n_D 1.603, soluble in 2.4 vols. of 70 per cent. alcohol. It contains 86 per cent. aldehydes. The entire oil (heavy and light fractions) would contain 68 per cent. aldehydes.

Citronella Oil. The exports of citronella oil from Ceylon[2]) totalled 1197507 lbs., in 1917, representing a value of 1173164 Rupees, as compared with 1443550 lbs. to the value of 1378519 Rupees, in 1914. The most important countries of destination were: —

	1914 lbs.	1914 Rup.	1917 lbs.	1917 Rup.
United States	530609	454567	713864	703766
Great Britain	615509	454567	279682	280705
Australia	111899	90946	121748	116432
Japan	21501	17190	37297	35550
India	10335	9029	26212	19389
France	25046	24988	11303	11575

Of Java oil, the following quantities were exported, in 1918: —

United States	87993	kos.
Singapore	45654	„
Japan	80867	„
other countries	13610	„
total	228124	kos.

In the beginning of 1918, the price in Java was about fl. 1.75, so that it was no longer remunerative for most of the factories. Towards the end of the year, it rose to about fl. 2.10 and is now fl. 4.— (beginning of October) for good quality c. i. f. European port.

A sample of Ceylon citronella oil, sent to us for examination, proved that the fakers are more daring now than ever, for the constants were so far from normal, that the article betrayed at once its being adulterated. It behaved as follows: $d_{15°}$ 0.9539, α_D + 5° 18′, total geraniol (geraniol + citronellal) 34.4 per cent., soluble in 1.5 vol. and more of alcohol 80 per cent. Only the solubility is right, the sp. gr. being far too high, the

[1]) *Bull. Imp. Inst.* **16** (1918), 146; *Perfum. Record* **10** (1919), 18. — [2]) *Perfum. Record* **9** (1918), 304.

rotation to the right instead of to the left and the content of total geraniol insufficient altogether, for it amounts to 54 per cent. at least in the normal commercial quality. Besides, some alcohols that have nothing to do with citronella oil, seem to have influenced the determination of the total geraniol, so that the content of real total geraniol would be still lower than indicated above. Hence, the falsification is very considerable and the smell indicates that a camphor oil fraction has been added.

Some time ago, K. Kafuku[1]) reported on the properties of a citronella oil distilled in Formosa. Now S. Furukawa[2]) mentions such an oil, but which has a considerably higher density (d 0.9601). The contents of total geraniol amounted to 22.15 per cent., that of total citronellal to 11.05 per cent. In his opinion, the Formosa oil is therefore of less value in perfumery than the Java or Ceylon products. It resembles in its composition the *Ogarugaya* oil, from a variety of *Andropogon Nardus*, L., growing in Japan.

Furukawa found in the Java oil eugenol, chavicole (?) and three acids, including citronella acid. Nothing is mentioned in the abstract, however, as to how the presence of these bodies was proved.

Regarding the distillation of Java citronella oil, see p. 81 of this *Report*.

Clove Oil. According to the last British Colonial Report[3]) the area under clove cultivation in Zanzibar and Pemba is estimated, this year, at 52000 acres with about 4700000 bearing trees. The large plantations are in the hands of Arabian land-owners, with but a few exceptions where the proprietors are Hindoos. The yield varies considerably, as the trees give specially abundant crops every 3 or 5 years. The annual average for the last years was about 14000000 lbs. The largest crop was that of 1911/12 with 28000000 lbs., 20000000 of which were supplied by Pemba, whereas the smallest was that of 1912/13 with only 4750000 lbs., Pemba's share being 3500000 lbs.

The prices fluctuate of course according to the yield. In the last years, it was between Rs. 8.8 and Rs. 27.9 per frasilah of 35 lbs. The Government levies a tax of 25 per cent. on all the cloves exported. The deliveries of the crops 1916/17 (1st July 1916 to 30th June 1917) and 1917/18 (up to April 1918) were as follows: —

	1916/17	1917/18
Zanzibar	7305166 lbs.	2226686 lbs.
Pemba	10602200 „	7896671 „
Total:	17907366 lbs.	10123357 lbs.

The prices fluctuated during this time between Rs. 12.25 and Rs. 27.56, for Zanzibar, and between Rs. 10.37 and Rs. 27.25, for Pemba (per frasilah of 35 lbs.). The high price was due to the favourable economical conditions in India, whose demand it was impossible to satisfy completely, on account of diminishing deliveries.

For obvious reasons, it was impossible to distil considerable quantities of cloves in Germany, during the war and some time will be required until the present scarcity of clove oil for home consumption can be remedied.

Oil of Coleus amboinicus. The *labiata Coleus amboinicus*, Lour. (*C. carnosus*, Hassk.) is one of the remedies most appreciated by the natives of Java. The leaves have a

[1]) *J. Chem. Ind.*, Tokyo **19** (1916), 411; *Journ. Soc. Chem. Industry* **37** (1916), 865; *Report* October **1917**, 15. — [2]) *J. Chem. Ind.*, Tokyo **21** (1918), 515; *Journ. Soc. Chem. Industry* **37** (1918), A 716. — [3]) *Chemist and Druggist* **91** (1919), 739.

peculiar aromatic odour. They contain only 5 per cent. of dry substance and very little essential oil; according to W. G. Boorsma[1]) only 0.055 per cent.

F. Weehuizen[2]) obtained from 120 kos. of fresh herb about 25 cc. of oil[3]), which scanty yield is explained in part by the presence of stalks, which do not contain any oil.

Half the oil dissolves in 5 per cent. soda lye, the phenol recovered from the lye being recognized as carvacrol. The nitroso compound prepared by Klages' method melted between 151 and 152°. In order to obtain the phenylurethane, Weehuizen heated 1.5 gram of the phenol for an hour under a reflux condenser with a similar quantity of phenyl*iso*-cyanate and about 10 cc. of a petroleum fraction[4]) boiling between 170 and 200°. After exposure to a low temperature, a white mass of crystals separated, which was washed with light petroleum (b. p. 80 to 100°) and then recrystallized from it. The carvacrolphenylurethane thus obtained melted between 134 and 135°, which tallies with Goldschmidt's[5]) indication, but not with that of Gildemeister[6]), according to which its m. p. is 140°.

By way of check, Weehuizen prepared the phenylurethane from carvacrol of other origin according to above method as well as by simply allowing a mixture of carvacrol, phenyl*iso*-cyanate and the petroleum fraction to stand in the cold. In either case, he found the m. p. indicated by Goldschmidt.

Copaiba balsam Oil. The Imperial Institute[7]) examined a sample of copaiba balsam, obtained in Columbia from *Copaiba officinalis*. It yielded 45.5 per cent. of volatile oil (d 0.899; α_D — 21.65°). The balsam itself dissolved in light petroleum, leaving but a small residue, and furnished a transparent solution with a 10 per cent. spirit of ammonia. The volatile oil boiled between 255 to 270°; $n_{D25°}$ 1.497.

Oil of Cymbopogon javanensis. J. J. Hofmann[8]) investigated the oil of a *Cymbopogon* species, growing wild in Java, especially in Kedu, but which has not been described botanically up to now. The oil is pale yellow, very liquid and possesses an agreeable sweetish odour, more allied to the palmarosa type than to that of citronella; $d_{15°}$ 0.9747; α_D — 2°54'; $n_{D20°}$ 1.51352; viscosity 1.568, as compared with water (determined with the aid of Engler's viscosimetre); acid v. 1.25; sap. v. 30.9; id. after acetylation 155.1; total geraniol 48.2 per cent.; free alcohols 33.9 per cent.; insoluble in alcohol 60 per cent., soluble in 1.9 vol. alcohol 70 per cent., there being turbidity if another 3 vols. or more be added; soluble in 0.6 vol. alcohol 80 per cent., there being turbidity on addition of a further 2.8 vols. or more; easily soluble in alcohol 90 per cent., a slight turbidity occurring on addition of 6 vols. The solutions in ether, acetic acid ester, amyl acetate, nitrobenzene, amyl alcohol, benzyl alcohol and methyl alcohol are clear, but mixtures of the oil with light petroleum, benzene, xylene, chloroform, carbon disulphide and carbon tetrachloride are turbid[9]). The mixtures with paraffine or fatty oils were not completely clear. Furthermore, about 90 per cent. of the oil are soluble in 4 parts of a mixture of equal quantities of sodium salicylate and water[10]).

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[1]) *Pharm. Weekblad* **52** (1915), 1678. — [2]) *Recueil trav. chim. des Pays-Bas* **37** (1918), 355. — [3]) The specific gravity is not indicated. Supposing it was 1, the yield would have been about 0,02 per cent. — [4]) Comp. *p.* 130 of this *Report*. — [5]) *Berl. Berichte* **29** (1893), 2086. Goldschmidt recommends to prepare it in the presence of $AlCl_3$ (superfluous!) — [6]) *Arch. der Pharm.* **33** (1895), 188. — [7]) *Bull. Imp. Inst.* **16** (1918), 147; *Perfum. Record* **10** (1919), 18. — [8]) *Inaugural dissertation*, Leyden 1919. He calls the plant temporarily *C. javanensis*. — [9]) This is due to the fact that the oil contained water. Had it been dried with anhydrous sodium sulphate, there would have been clear mixtures. The same applies to those with paraffine and fatty oils. — [10]) *Bulletin de l'académie Royale de médicine de Belgique* of June 24th 1899.

The oil did not contain any nitrogenous compounds.

Under a pressure of 20 mm., it distilled between 100 and 170°, leaving a thick, resinous residue.

It contained traces of bodies resembling phenol and about 6 per cent. of compounds reacting with sodium disulphite. An inconsiderable part of these melted at 42°; b.p. about 270° (d 1.151; n 1.551). The smell of this body recalled vanilla and calamus oil; its phenylhydrazine melted between 110 and 112°. The product proved to be identical with methylvanillin (dimethylprotocatechualdehyde), which for the sake of comparison was prepared from potassium vanillate, methyl alcohol and methyl iodide and likewise melted at 42°. The phenylhydrazone also showed the m.p. indicated above. A mixture of synthetic and natural methylvanillin also melted at 42°.

It was possible also to isolate another aldehyde, most likely citral, with the aid of sodium bisulphite solution.

In the form of esters were present: formic acid (reactions with cerium nitrate, silver nitrate and mercury dichloride), butyric acid, valeric acid and caprylic acid. Their presence was established also by a microchemical method.

As to terpenes, l-α-pinene was present (m.p. of the hydrochloride = 126°).

Furthermore, the oil contains an alcohol of an agreeable rose-like odour, identical very probably with citronellol[1]). It reacts with calcium chloride and boils at 225°, d 0.8848; the m.p. of the silver compound of the phthalic acid ester is 124°. Geraniol is also one of the constituents (diphenylurethane melting at 77°, which low figure the author explains by an admixture of citronellol).

In the high-boiling fractions, methyl-*iso*-eugenol occurs (m.p. of the dibromide, 101°). A determination of the methoxyl revealed that the proportion was 30.5 per cent. of the oil.

Cypress Oil. A cypress oil received from France via a neutral country did not reflect any credit on its French manufacturer, for it was of an abominable quality. Contrary to the normal distillate, it was viscous, dark brown and had a resinous odour, which did not at all resemble that of true cypress oil. The constants were also far from normal, as the following comparison shows: —

	Oil in question	German destillates	French destillates
$d_{15°}$	0.9914	0.88 to 0.90	0.868 to 0.884
α_D	+ 29° 20′	+ 4 to + 18°	12 to + 31°
solubility in alcohol 90 per cent.	0.3 vol.	2 to 7 vols.	4 to 7 vols.
acid value	20.5	1.5 to 3.0	up to 2
ester value	42.9	13 to 22	3 to 14

Obviously, the product was strongly resinified and it made the impression of a mixture of various remnants, which had been standing about for years and were absolutely spoiled. In consequence, even the rectification with steam did not lead to an oil fit for use. The constants then came somewhat nearer to the normal ones, but the smell was still unsatisfactory and conveyed the idea of considerable decomposition. What degree the resinification had reached, could be deduced from the fact that the rectification yielded only 50 per cent. We have not ascertained whether the oil was adulterated besides, but this is a minor detail, as it was unfit for use in any case. The firm who supplied the stuff did not admit frankly to our middleman that the oil was bad, but tried to waive the question by subterfuges meant to be scientific, but which really were absolutely void. We have given the answer deserved.

[1]) However, citronellol does not react with calcium chloride.

Essential Oils, Sicilian and Calabrian.

Bergamot Oil is getting scarce and the coming crop is anticipated to be middling only.

Lemon Oil is offered abundantly just now, the tendency being firmer, however, since the exports from Sicily have become brisker. The prospects of the new crop are supposed to be favourable.

Orange Oil, sweet. There are scarcely any stocks left and the prospects are not very satisfactory. The yield of this year's crop is reported to be unfavourable and as a probably very large export of oranges in all directions is to be expected, it is feared that there will be little material left for obtaining oil.

Orange Oil, bitter. Reliable qualities are not to be had, except perhaps at fabulous prices. Fruits of the new crop are now contracted for at *L.* 50.— per thousand and 1 ko. of salted bitter oranges costs *L.* 1.—, prices which indicate that a very bad crop is expected.

Mandarin Oil. Now and then, small quantities are offered at fantastic prices and it is taken for granted that the crop will prove insufficient for the large export demand.

Happily we are now able to append the statistics for 1914 to 1918, which it was impossible to obtain during the war. A clear idea cannot yet be formed of the conditions of the market, the less so as it is only a few months ago that business began to take a normal turn again.

Exports in 1914 to 1918.

I. 1914.

Orange Oil.

Destination	quantity	value
France	kos. 9347	
Great Britain	„ 8820	
Russia	„ 278	
Switzerland	„ 2444	
United States of North America	„ 7734	
Other countries	„ 14215	
Total:	kos. 42838	Lire 813922

Bergamot Oil.

France	kos. 22069	
Great Britain	„ 12478	
Russia	„ 1657	
Sweden	„ 95	
Switzerland	„ 1335	
United States of North America	„ 12875	
Other countries	„ 11248	
Total:	kos. 61757	Lire 2470280

Lemon Oil.

Destination	quantity	value
France	kos. 42525	
Great Britain	„ 172056	
Russia	„ 5611	
Switzerland	„ 1096	
Australia	„ 27937	
Argentina	„ 3177	
United States of North America	„ 244530	
Other countries	„ 106066	
	Total: kos. 602998	Lire 10853964

Mandarin Oil.	Other Oils.
kos. 981 . . Lire 37278	kos. 378 . . Lire 9072

II. 1915.

Orange Oil.

Destination	quantity	value
France	kos. 12781	
Great Britain	„ 13057	
Russia	„ 1192	
Switzerland	„ 7208	
United States of North America	„ 21493	
Other countries	„ 14941	
	Total: kos. 70672	Lire 1130752

Bergamot Oil.

France	kos. 38850
Great Britain	„ 17764
Russia	„ 3134
Sweden	„ 608
Switzerland	„ 4724
United States of North America	„ 26064
Other countries	„ 14409
Total:	kos. 105553 . . . Lire 3377696

Lemon Oil.

France	kos. 57444
Great Britain	„ 268331
Russia	„ 3330
Switzerland	„ 27897
Australia	„ 49575
Argentina	„ 7074
United States of North America	„ 255268
Other countries	„ 75092
Total:	kos. 744011 . . . Lire 9300137

Mandarin Oil.	Other Oils.
kos. 1207 . . Lire 55522	kos. 424 . . Lire 9328

III. 1916.

Orange Oil.

Destination	quantity	value
France	kos. 14998	
Great Britain	„ 15525	
Russia	„ 5633	
Switzerland	„ 18960	
United States of North America	„ 30335	
Other countries	„ 10606	
Total:	kos. 96057	Lire 2593539

Bergamot Oil.

France	kos. 46474	
Great Britain	„ 31440	
Russia	„ 13007	
Sweden	„ 9573	
Switzerland	„ 17101	
United States of North America	„ 22101	
Other countries	„ 17469	
Total:	kos. 157165	Lire 6758095

Lemon Oil.

France	kos. 39171	
Great Britain	„ 161160	
Russia	„ 20376	
Switzerland	„ 56208	
Australia	„ 23216	
Argentina	„ 7169	
United States of North America	„ 289001	
Other countries	„ 59221	
Total:	kos. 655522	Lire 6227459

Mandarin Oil.	Other Oils.
kos. 1839 . . Lire 130569	kos. 839 . . Lire 25470

IV. 1917.

Orange Oil.

Destination	quantity	value
France	kos. 22694	
Great Britain	„ 9416	
Russia	„ 55	
Switzerland	„ 160	
United States of North America	„ 32061	
Other countries	„ 7961	
Total:	kos. 72347	Lire 2532145

Bergamot Oil.

Destination	quantity	value
France	kos. 57545	
Great Britain	„ 29557	
Russia	„ 56	
Sweden	„ 3979	
Switzerland	„ 604	
United States of North America	„ 33601	
Other countries	„ 8457	
	Total: kos. 133799	Lire 8696935

Lemon Oil.

France	kos. 62370	
Great Britain	„ 121584	
Russia	„ 100	
Switzerland	„ 2031	
Australia	„ 21860	
Argentina	„ 5615	
United States of North America	„ 280439	
Other countries	„ 28487	
	Total: kos. 522486	Lire 5747346

Mandarin Oil.		Other Oils.	
kos. 2450	Lire 171500	kos. 1369	Lire 54760

V. 1918.

Orange Oil.

Destination	quantity	value
France	kos. 102184	
Great Britain	„ 197391	
Russia	„ —	
Switzerland	„ 248	
United States of North America	„ 16371	
Other countries	„ 6626	
	Total: kos. 312820	Lire 10948700

Bergamot Oil.

France	kos. 182564	
Great Britain	„ 593325	
Russia	„ —	
Sweden	„ —	
Switzerland	„ 2128	
United States of North Amerika	„ 33441	
Other countries	„ 10351	
	Total: kos. 821809	Lire 53417585

Lemon Oil.

Destination		quantity	value
France	kos.	437263	
Great Britain	„	198234	
Russia	„	—	
Switzerland	„	2963	
Australia	„	25027	
Argentina	„	20644	
United States of North America	„	254992	
Other countries	„	690617	
Total:	kos.	1629740	Lire 17927140

Mandarin Oil.		Other Oils.	
kos. 2162	Lire 151340	kos. 1240	Lire 49840

The prices therefore fluctuated as follows (Lire per ko.): —

	1914	1915	1916	1917	1918
Orange Oil	19	16	27	35	35
Bergamot Oil	40	32	43	65	65
Lemon Oil	18	12.5	9.5	11	11
Mandarin Oil	38	46	71	70	70

Further statistical notes are to be found on p. 79 of this *Report*.

Bergamot Oil. The trade no sooner begins to revive a little than the fakers are at work again, as a sample of bergamot oil shows, which recently reached us. It was too small for a complete analysis, but as revealed by quite a cursory examination the adulteration was considerable. The rotation which with a normal oil lies between + 8 and + 22° was + 36° 30′. The specific gravity was too low (0.8802) and the ester value insufficient, being only 30.4 per cent., as compared with at the least 34 per cent. for a good commercial quality. Obviously, it was still lower in reality and had only been raised by adding another ester, for the difference between saponification value (89.2) and acid value II (62.5) amounted to 26.7, whereas with pure bergamot oil it ought not to go beyond 10. This points to phthalic ester having been used, but the smallness of the sample did not permit of going further into the matter. The other adulterants were most likely terpenes of high rotatory power.

Lemon Oil. We have had to examine various samples of lemon oil which, if not altogether artificial products, were at least strongly adulterated. One of them had the following constants: $d_{15°}$ 0.8573, $\alpha_{D20°}$ + 61° 55′, α_D of the first 10 per cent. of the distillate + 63° 54′ residue after evaporation 0.8 per cent. Specific gravity and rotation were within the limits for lemon oil, but the behaviour of the first 10 per cent. of distillate were abnormal in that their rotation is higher than that of the original oil, whereas the reverse happens with genuine lemon oil. Furthermore the residue after evaporation was far too low and did not show the characteristic waxlike consistency, but was resinous. As in addition, the smell was strange and disagreeable, not at all similar to that of lemon oil, the reader will be able to conclude by himself that the concoction was an absolute failure.

The same applies to another oil, which made itself conspicuous by its high specific gravity and also had a disagreeable odour, reminding us somewhat of amber oil. In this case, the quantity at our disposal was so small, that we were unable to prove other irregularities.

For curiosity's sake, we would mention a so-called lemon oil from Chemnitz (Saxony). The only similarity was in the colour, for this "oil" consisted otherwise only of water.

Great caution in buying terpeneless lemon oil is recommended by W. Scholvien[1]), who writes as follows: "It must be pointed out as a warning that of late so-called sesquiterpeneless lemon oil (30 fold strength) has been offered at ℳ 2400.— per kilo and apparently sold on a fairly large scale. The article in question is grossly adulterated, the specific gravity being 1.07 (against 0.90 to 0.91[2]) for a normal quality), owing most likely to the addition of a heavy ester. Even a layman can easily prove this falsification, as such an oil sinks in water, whereas the normal product would float."

We believe we are not mistaken in supposing that phthalic acid ester has something to do with it, this product now being a favourite adulterant, as a good number of instances in this *Report* testify.

Orange Oil, sweet. We received from Wiesbaden a sweet orange oil which behaved singularly, as follows: $d_{15°}$ 0.8528, $\alpha_{D20°}$ + 82° 54′, α_D of the first 10 per cent. of the distillate + 76° 14′, residue after evaporation 2.9 per cent. The specific gravity, it is true, is within the correct limits, but the optical rotation ought to be between + 95° 30′ and + 98°, being the same, or but a trifle lower, for the first 10 per cent. of the distillate. Besides, the residue after evaporation was suspicious, being viscous instead of waxlike. The only explanation for these deviations is that either the oil was grossly adulterated or an artificial product. It is to be hoped that substitutes of this nature, which one met rather often in the last few years, will soon be great rarities.

J. A. Liems[3]) has published an article on the cultivation of *"agrumen"* fruits in Surinam, according to which it is remunerative and seems to have a promising future. In the main, oranges are cultivated, the fruit obtained being of very good marketable quality. Apparently no oil has been manufactured there, so far.

There are no further details in the discussion at our disposal.

Diseases of "agrumen" trees. — We have already several times aquainted our readers with diseases of the cultivated *Citrus* species[4]) and wish in this connection to mention a notice on a new bacterial disease of certain such trees, published in an English periodical[5]). The disease has been observed for the first time in California. It was found to be due to a bacterium, to which the name *Bacterium citrarefaciens* was given, whereas the disease itself received the name of Citrus Blast. Infection is chiefly confined to new spring growth or unseasoned wood of the previous year, and occurs specially at the junction of the petiole and blade of the leaf. The tips of the very young leaves and tender shoots are also easily affected. The infected leaf turns pale yellow, then darkens irregularly in spots, wilts, shrivels and finally dries. Once established, the disease rapidly progresses towards the older wood, although this is more resistant. The young shoots are often killed back to the older wood, including part of the bark

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[1]) *Deutsche Destillateur-Ztg.*, **40** (1919), 354. — [2]) These figures seem to be based on E. Böcker's notes on terpeneless and sesquiterpeneless lemon oil in the *"Wallach-Festschrift"* (Göttingen 1909, p. 228). He there indicates 0.895 to 0.909. We have observed lower values, sometimes, with our own products. — [3]) *Bulletin van het Department van den Landbouw; Perfum. Record* **9** (1918), 296. — [4]) Comp. *Reports* October **1915**, 65, October **1916**, 99. — [5]) *Agricultural News; Perfum. Record* **9** (1918), 178.

about the base of the shoot, where characteristic lesions are formed. If the disease is virulent, it may attack branches grown in the previous season as large as 1/2 in. in diameter, killing them back for the length of several feet. Conditions being favourable — which is the case when warm damp weather prevails —, the disease can cause serious damage within a few days. In California these conditions rarely occur, save in spring, and in the following dry season the disease diminishes. A pinkish resinous gum or bacterial slime is often exuded and afterwards the lesions and all the dead tissues turn a characteristic dark red colour. The dead twigs when dry are very tough and hard. Little by little, scab-like masses of wound-callus form where the lesions were and, on falling off later on, leave typical scars.

Remedies against this disease are so far unknown.

Eucalyptus Oil. As per a notice dated 12. X. 1918 in an English periodical[1]), many distilleries in Victoria will have to close, in case exports are not made possible. In consequence, the people concerned in Melbourne have founded a Central Overseas Export Committee, partly with the aim of procuring tonnage for eucalyptus oil. In autumn, there were considerable stocks of eucalyptus oil in London, 5000 cases containing 250000 to 280 lbs. having arrived during the first half of 1918. Since June, however, extremely little oil had arrived.

During the war, the quotations were comparatively low. In July 1914, large quantities of oil answering the pharmacopœia were to be had in Mincing Lane at 1/3 lb., and end of July 1917 the price was not higher than 2/3 lb. Since then it has risen to 4/3 lb. for the middle of October 1918.

The oil is generally shipped in petroleum tins, which often arrive leaking.

On page 28 of our *Report* of October **1918**, we briefly referred to the planting of eucalyptus trees in the Federated Malay States, mentioning that seedlings grew rapidly which belonged most likely to the species of *Eucalyptus citriodora*, but that it would be necessary to see the flowers before a conclusive botanical determination could be made. The trees in question have blossomed meanwhile and it resulted that they really belong to the *E. citriodora* species, not to *E. Backhousiana*, as was thought possible at the time. In three years from sowing, the trees attained a height of 45 feet, and appeared quite healthy and were growing vigourous. Rearing this kind from seeds succeeds excellently in the Malay States[2]).

Eucalyptus trees have been planted in various parts, also in British India, as stated on page 27 of our *Report* of October **1918**. *Eucalyptus tereticornis* and *E. crebra* are among the eucalypts cultivated in the trial-garden at Kaunli (Dehra Dun) the oils of which two species were distilled there.

According to an article by T. P. Ghose[3]), the leaves and short twigs of *Eucalyptus tereticornis* contained 22.75 per cent. of moisture and 0.66 per cent. of essential oil (0.86 per cent. calculated on dry material). The crude oil was dark brown and yielded on rectification a yellow oil of pleasant but not characteristic smell. It distilled between 155 and 210°, leaving a residue of 24 per cent. The properties of the rectified oil were: $d_{16°}$ 0.903, α_D — 22.26°, $n_{D16°}$ 1.4905, sap. v. 27.25 (after removal of the free acid and

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[1]) *Chemist and Druggist* **90** (1918), 811. — [1]) *Perfum. Record* **9** (1918), 242. — [2]) *Perfum. Record* **10** (1919), 145.

aldehydes), ester v. after acetylation 63.45, soluble in 16 vols. of alcohol 70° and in 1.9 vol. of alcohol 80°. The eucalyptole fraction boiling between 170 and 190° (53 per cent., $d_{16°}$ 0.874, α_D — 8.56°, $n_{D16°}$ 1.4865) yielded no solid compound with phosphoric acid. It contained 10.4 per cent. of eucalyptole, as treatment with a 50 per cent. resorcinol solution showed. The oil contained 8.4 per cent. of aldehydes but no phellandrene.

Leaves and short twigs of *E. crebra*, likewise from Kaunli, contained 33.0 per cent. of moisture and 0.31 per cent. of essential oil (0.46 per cent. calculated on dry material).

The oil distilled over between 170 and 240°, leaving 41 per cent. of residue. The rectified product ($d_{16°}$ 0.899, α_D — 3.24°, $n_{D16°}$ 1,4673, acid v. 6.8, ester v. after acetylation 55.24, soluble with turbidity in 15 vols. of alcohol 80 per cent.) obviously did not contain any eucalyptole, for there was no crystalline deposit with a 50 per cent. resorcinol solution. The oil was free from phellandrene, aldehydes and ketones.

Both oils do not answer the requirements of the British Pharmacopœia, are unfit for medicinal use and can only come into consideration perhaps for perfuming purposes, owing to their agreeable smell.

We would add that as far as *Eucalyptus tereticornis* is concerned, the foregoing details tally fairly well with Baker and Smith's remarks, according to whom, however, the oil of *E. crebra*, F. v. M., contains much phellandrene and cineole[1]) *i. e.* just the reverse of what is said in Ghose's article.

According to an English periodical[2]), the experimental eucalyptus plantations in the Khasi and Jaintia Hills, Assam, were not successful owing to the attacks of white ants (termites). The localities were apparently too low and unsuitable, at any rate, for *Eucalyptus globulus*. In consequence, it has been advised to repeat the experiments at the elevation of Shillong.

The index of refraction in testing eucalyptus oils. — Generally speaking, the index of refraction is of little importance in examining essential oils. H. G. Smith[3]) thinks, however, that it is otherwise with regard to certain eucalyptus oils. His article contains many other noteworthy remarks on Australia's eucalyptus oil industry. He mentions that the methods of distillation have been greatly improved in the last years and that far more attention than formerly is paid to the homogeneous nature of the material distilled. In consequence, the oils show fairly constant properties. It becomes more and more customary to sell the oils of definite eucalypts under their botanical name, such as oil of *Eucalyptus polybractea*, *E. Smithii*, *E. dives*, *E. Macarthuri*, &c. In this way, it is possible to arrive at the desired uniformity of the products. As soon as the advantages of this method have been generally recognized and it works accordingly, it will be no longer necessary to mix the oils of several species in order to arrive at a definite class of product. This would be a benefit for the whole industry.

Smith thinks that the refractometre is important not only for the examination of the oils, but that the determination of the refraction makes it possible to discover in the oils constituants hitherto unknown. Butyl butyrate for example was found in this way in the oil of *Eucalyptus Perriniana*[4]), owing to the very low refractive index (1.4538 at 10°) of the lowest boiling fraction. Meanwhile, this ester has been found in many allied species.

The species, whose leaves are distilled most in Australia now are *Eucalyptus polybractea*, *E. australiana* and *E. dives*.

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[1]) Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd ed., vol. III, pages 277 and 294. — [2]) *Perfum. Record* **9** (1918), 207. — [3]) *Journ. Soc. chem. Industry* **37** (1918), 272 T. — [4]) *Proceed. Royal Soc. of N. S. W.*, December **1914**; comp. *Report* October **1913**, 57.

Smith ascertained the following properties for the crude oil of *E. polybractea:* $d_{15°}$ 0.9245 to 0.9292, α_D — 0.3 to + 0.8°, $n_{D20°}$ 1.4624 to 1.4633; for the rectified oil: $d_{15°}$ 0.9195 to 0.9300, α_D — 0.2 to + 0.5°, $n_{D20°}$ 1.4586 to 1.4624. It dissolves in 1.05 to 1.1 vol. of alcohol 70 per cent. (by weight = 76.9 per cent. by volume), the solubility being very constant. Considerable quantities of this oil are now exported to the United States.

Smith ascribes the small rotation to the left, shown by some oils, to the presence of aromadendral. The high index of refraction is caused by a considerable content of eucalyptole.

Large quantities of an excellent oil have been distilled during the last three or four years in the Nerrigundah and Yowrie districts of New South Wales from *Eucalyptus australiana,* formerly known as *E. amygdalina*[1]).

This species seems to have disappeared from its elevated original territories and to have settled down in lower regions, where it yields an oil almost free from phellandrene but all the richer in cineole[2]). The oil distilling over during the first hour is collected separately and sold for pharmaceutical purposes. It contains 70 per cent. of cineole or more. The oil distilled after that serves for treating ores.

The oil obtained during the first hour has the following properties, according to Smith: $d_{15°}$ 0.9186 to 0.9220, α_D — 1.2 to + 1.7°, $n_{D20°}$ 1.4617 to 1.4636. Two oils distilled after the first hour showed: $d_{15°}$ 0.9096 and 0.9160, α_D + 2.0 and + 3.6°, $n_{D20°}$ 1.4710 and 1.4711. The trifling rotation to the left, observed sometimes with the oil of *Eucalyptus australiana,* is caused by the presence of phellandrene.

The index of refraction of lævogyrate oils is a little higher than that of the dextrogyrate. The oil distilling over after the first hour has a higher index of refraction; the cineole content is not even one fourth of that of the oil obtained during the first hour. Ready solubility in alcohol characterizes also those oils of *Eucalyptus australiana,* rich in phellandrene, which have been distilled in high regions.

The oil of *Eucalyptus dives* chiefly consists of *l*-phellandrene, is therefore strongly lævogyrate and contains as a rule less than 5 per cent. of cineole. It has often been exported to Europe as Amygdalina oil. There is a certain excuse for this, as *E. dives* was looked upon formerly as a variety of *E. amygdalina.*

The oil of *E. dives* is considered the most appropriate for the metallurgical flotation process. $d_{15°}$ 0.8928 to 0.9020; α_D — 55.4 to 69.8°; $n_{D20°}$ 1.4798 to 1.4809.

Fennel Oil. H. Blin[3]) reports that fennel growing extended considerably in France, previous to the prohibition of absinthe, decreed a few years ago, in the preparation of which liqueur fennel acted an important part. It is carried on in the Rhône valley, especially on the right bank, in cool sites, not far from Avignon and in the neighbourhood of Montélimar. The absinthe industry consumed such quantities of fennel that the Rhône valley, the Provence and the Languedoc were unable to satisfy the demand. About 2000000 kos. had to be imported via Marseilles, three quarters of which came from Saloniki and one quarter from India.

The fennel plant is propagated by lateral shoots, but it is always advantageous to renew the plantations from seed and to cultivate the transplanted seedlings. The site must be open, alluvial soil without excessive moisture being preferred. It must be prepared by deep digging, followed by harrowing and rolling. After the autumnal

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[1]) See *Report* October **1917**, 18. — [2]) Comp. Baker and Smith, *Proceed. Royal Soc. of N. S. W.*, December **1915**. — [3]) *Parfum. moderne; Perfum. Record* **9** (1918), 275.

rains, abundant quantities of stable-dung are spread on it, when the harrowing is repeated, and the seeds are sown in February in drills 10 cm. deep and 75 cm. apart. Previously, a little powdered press-cake is strewn in the furrows which, after having received the seeds, are covered by ploughing. About 10 to 15 kos. of seeds are required per hectare. End of April, when the plants are from 8 to 10 cm. high, they are thinned out, so that there is a space of 10 to 15 cm. between them. In June the ground is dug over and harrowed with a very light harrow.

The harvest begins in August, as soon as the fruits ripen. The ripening proceeds from the centre of the umbels outwards and lasts throughout the month.

The ripe fruits as collected are stored in a dry place and, when the harvest is over, separation from stalks, &c., is effected by means of a roller, the debris being removed by a current of air.

The most important centres of production are situated in the Department of the Gard, where fennel is grown in many parishes, in some the great and in others the small variety. In certain villages, it is the custom for the merchants to supply the peasants with the seed and to contract for the crop at a fixed price. Fennel is also grown in Bourg-Saint-Andéol in the Ardêche, but the distilleries of Lyons, Avignon, Marseilles, Grenoble, Valence and Montpellier are supplied almost entirely by the crops of the Gard.

The principal markets are at Pont-Saint-Esprit, Orange and Nîmes. In normal years, the Department of the Gard alone furnishes to the factories about 300000 kilos of fennel fruits.

For our own distillation, plantations near Lützen provide at present the fennel seed required, there being no imports as yet from Galicia, which mainly supplied the market formerly. The crop is rather late this year and is not generally considered favourable. In consequence, the prices are so high that it is hardly possible to think of distilling on a large scale. Whereas last year fennel seed cost ℳ 165.— per 100 kilos, on an average, the holders now ask for ℳ 390.— to ℳ 400.—.

Ginger Oil. A pungent substance, zingerone, a resolution product of the gingerol, originally contained in the drug, can be prepared from the ginger rhizomes[1]). H. Nomura[2]) communicates that on distilling the pungent constituents of Japanese ginger, another substance can be obtained in addition to zingerone. He calls it shogaol ($C_{17}H_{24}O_3$); b. p. 231 to 238° (15.5 mm.), $d_{25°}$ 1.0448, $n_{D25°}$ 1.52467. It contains a methoxyl and a hydroxyl group and was accordingly converted into a monomethyl, monoethyl and monoacetyl derivative. Presumably, it also contains a keto group and an ethylene compound, for it was possible to hydrogenize it with the aid of platinum black and hydrogen into a dihydro derivative.

Together with F. Nozawa[3]), Nomura tried to find out which structural properties imply the characteristic taste of zingerone (*4*-hydroxy-*3*-methoxyphenylethylmethylketone), by preparing a number of phenylethylmethylketones, which contain hydroxyl or methoxyl groups in the benzene nucleus. It resulted that such ketones as contained hydroxyl in para-position to the keto group of the lateral chain, especially those derived from vanillin, resembled the zingerone in taste. The degree of pungency is influenced by the position of the hydroxyl with regard to the lateral keto-chain and is increased by the presence of an *m*-methoxyl group. The influence of the hydrocarbon radical

[1]) Comp. *Report* October 1918, 29. — [2]) *Sci. Rep. Tohoku Imp. Univ.*, 67; *Journ. Soc. chem. Industry* **37** (1918) A. 606. — [3]) *Sci. Rep. Tohoku* **7** (1918), 79; *Journ. Soc. chem. Industry* **37** (1918), A. 606.

connected with the keto group upon the taste is scarcely any greater than that of the position of the hydroxyl, for the *4*-hydroxy-*3*-methoxyphenylethylphenylketone resembles zingerone in taste.

Ginseng-root Oil. According to W. Sakai[1]), the ginseng-root *(Panax Ginseng*, C. A. Mey.; *Araliaceæ)*, much esteemed in China as an aphrodisiac, contains as principal constituent of the parts soluble in ether a terpene-like body called "panacene". B. p. 105 to 110° (15 mm.); d 0.925. It has a feebly narcotic action on the brain centres, but stimulates the vasomotoric and respiratoric centres, thus raising the blood pressure and rate of respiration.

Grape fruit Oil. The tendency to use the by-products of the American citrus industry[2]) induced H. P. Zoller[3]) to investigate the chemical constituents of the grape fruit. He reports on his work in an article called: "Some of the constituents of the American grape fruit *(Citrus decumana)*", in which we find an analysis of the oil of the grape fruit peel, the composition of which was almost unknown so far. In the sorting and grading of the thousands of tons of grape fruit, representing a season's crop, many tons of culls are allowed to rot. Certain of the producing companies are now seriously contemplating the isolation of the by-products.

According to Zoller, the name grape fruit originated from the fact that the fruit commonly occurs on the trees in large clusters, somewhat resembling grapes. The term "pomelo" has been applied and adopted by the U. S. Department of Agriculture, American Pomological Society, &c., without appealing to the public. The English of Ceylon and India call it pomelow, a name probably derived from the Latin *"pomum melo"*. The name of *"Pompelmuse"* (in Dutch *"Pompelmoes"*) has been used already by Rumphius. The term shaddock has crept into the literature as a synonym for grape fruit in honour of a certain British sea-captain, who is said to have introduced the fruit into the West Indies from Java early in the eigteenth century. It is interesting to note that in Java, which is the acknowledged home of the grape fruit, there are two varieties. One is small and bitter, though edible, and grows in the lower coastal regions of the island. The other variety is much larger, intensely bitter, with a dark-yellow or red pulp; it grows at much higher altitudes and is known there as the non-edible variety. The bitter principle in both varieties is identical, which would lead to their classification as sub-varieties under *Citrus decumana*. It is likely that the term shaddock applies more specially to the larger and non-edible variety.

Just at what particular date the grape fruit was introduced into the U. S. of North America is not known. It is not improbable that the Spaniards first introduced the fruit into Mexico and Central America. Florida and California practically comprise the entire source of grape fruit in the United States. Numerous varieties of grape fruit have resulted from the efforts of the citrus growers and horticulturalists.

The oil examined by Zoller had been obtained from the peels of the cultivated varieties Indian River, De Soto and Excelsior. The oil cannot be obtained by simple pressing, as it does not separate easily from the liquid thus produced. The method finally adopted was to cut the peel finely mix it with an equal quantity of water and

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[1]) *Tokyo Igakukai* **31** (1917), 1; *Chem. Abstracts* **12** (1918), 2033. — As per *Perfum. Record* **10** (1919), 20. — [2]) Comp. R. T. Will, *Journ. Industr. Engin. Chemistry* 8 (1916), 78; F. A. Mc. Dermott, *ibidem* 136; *Report* October **1916**, 19, 24. — [3]) *Journ. Industr. Engin. Chemistry* **10** (1918), 364.

distil with steam under reduced pressure. It may become necessary to use a second receiver, cooled with a brine-ice mixture.

The oil, after having been washed with normal Na_2CO_3 solution and dried with anhydrous sodium sulphate, smelled strongly of citral; $d_{20°}$ 0.845 and 0.860; $\alpha_{D20°}$ +72.5 and +78.5; $n_{D20°}$ 1.4750 and 1.4785. Under a pressure of 12 mm, the oil boiled at from 48 to 115°. The presence of α-pinene could be proved in the fractions boiling between 48 and 52° and between 52 and 70°. The nitrosochloride melted between 102 and 103°, the hydrochloride at 132°. The latter fraction also contained *d*-limonene, b.p. 175°; $\alpha_{D20°}$ +38°; tetrabromide, m.p. 104°. This fraction did not yield any semicarbazone with semicarbazide-HCl and sodium acetate.

The fraction boiling at from 70 to 85° (12 mm.) contained linalool in addition to limonene. The linalool was characterized by shaking it with 5 per cent. sulphuric acid, when terpene hydrate formed (m.p. 116°). The oxidation of the linalool to citral was impossible in this connection, since citral was in the succeeding fraction in large quantity.

Zoller proved the presence of citral in the fractions boiling between 85 and 115°; the semicarbazide melted at 165°.

As the fraction boiling between 100 and 115° could not contain any linalool, judging by its boiling point, but on being shaken with 5 per cent. sulphuric acid deposited terpene hydrate, Zoller assumed that geraniol was present. It may be expected that both linalyl and geranyl acetate are present too.

Mixed with 30 per cent. of alcohol, the oil seems to keep a long time.

Oil of Jasminum odoratissimum, L. From fresh *Shuei*-flowers *(Jasminum odoratissimum,* L.; *Oleaceæ),* cultivated in Formosa and used for perfuming tea, R. Tsuchihashi and S. Tasaki[1]) extracted with light petroleum 0.277 per cent. of a concrete oil, which upon maceration with alcohol yielded 0.116 per cent. of essential oil and 0.166 per cent. of floral wax. *Enfleurage* did not lead to any result. The oil was a reddish-brown liquid; $d_{15°}$ 0.9309, $\alpha_{D15°}$ +5.64°, $n_{D15°}$ 1.4845, ac d v. 5.85, sap. v. 92.25, sap. v. after acetylation 186.20. The oil boiled at from 60 to 200°[2]). The following constituents were ascertained: 6 per cent. linalool, 6 per cent. linalyl acetate, 1.6 per cent. benzyl alcohol, 6 per cent. benzyl acetate, 10 per cent. indole and methyl anthranilate[3]). The higher-boiling fractions contained a diterpene or a sesquiterpene alcohol, which constituted about 57 per cent. of the oil. Jasmone was not present.

Kauri copal Oil. On dry distillation or with steam, kauri copal (from *Dammara australis,* Lamb.; *Pinaceæ*) yields an essential oil, which is but of little practical value. Nevertheless, we would mention that, according to an article published in trade-journals, progress is made in obtaining simultaneously from kauri trees crude oil, acetic acid, ammonia, pitch and "spirit-gum", a quickly drying adhesive substance, used in the main by hair-dressers and actors. As per the *Chemical Trade Journal* and the *Chemical Engineer*[4]), unlimited quantities are available. A company is said to have been granted the monopoly for 40000 acres, which constitute only a small portion of the forests available for the purpose. The yield of crude oil from 1 ton of refuse gum is estimated at 76 gallons, that of 1 ton of the wood at 168 gallons. It is

[1]) *J. Chem. Ind.,* Tokyo **21** (1918), 8117; *Journ. Soc. chem. Industry* **38** (1919), A. 117. — [2]) There is no indication of the pressure. — [3]) Nothing is said as to how the presence of these bodies was proved. — [4]) *Nachr. f. Hand., Ind. u. Landw.* **1918**, n°. 166, p. 8.

supposed that this industry will be very remunerative, although no large quantities of crude oil have been rectified so far and the real market-value of the article remains to be fixed.

Lavender Oil. The following result of the examination of a lavender oil sent us for inspection, may be interesting to our readers: $d_{15°}$ 0.9998, α_D — 0°44′, soluble in 1.2 vol. and more of alcohol of 70 per cent., acid v. 0.6, ester v. 226.4, acid v. II 47.6, difference between sap. v. and acid v. II 179.4. Of all these constants, only the acid v. and the solubility are normal, whereas the specific gravity is too high, the rotation too low and the ester v. of an incredible height, as it would correspond to an ester content of 79 per cent. As was to be deducted from the far too considerable difference between sap. v. and acid v. II (normally 3 at the most!) an ester of a non-volatile acid had served as an adulterant. It resulted that about 30 per cent. of the completely inodorous phthalic ester, now quite a fashionable adulterant, had been added, which explained the abnormally high ester value.

In another case, terpineol had been added. The sample of oil at our disposal was too small to characterize the terpineol otherwise than by its smell. The faker had dosed it so liberally that there was no possibility of making a mistake. The proportion of real lavender oil in the mixture was not more than 50 per cent., if so high, but we do not doubt that the "favourable" price attracted many a buyer. He who buys the ingredients, however, can prepare it much cheaper himself.

Lemongrass Oil. As to the cultivation of lemongrass oil in Java, see p. 82 of this *Report*.

Oil of Leptospermum flavescens var. citratum. Challinor, Cheel and Penfold[1]) describe a species of Leptospermum *(L. flavescens; Myrtaceæ)* occurring in New South Wales and Queensland, the *citratum* variety of which contains in its leaves from 1.73 to 1.85 per cent. of a pale amber-coloured volatile oil: d 0.8841, $\alpha_{D18°}$ + 3.6°, $n_{D20°}$ 1.4730, sol. in 2 vols. of 70 per cent. alcohol by weight. It contained 89 to 90 per cent. of aldehydes, consisting of citronellal and citral in approximately equal proportions. A small amount of an alcohol, possibly geraniol or citronellol, was found, and a phenol, the benzoate of which melted at 67°. There was also evidence of the presence of aromadendrene.

There is nothing stated in the abstract regarding the method by which the presence of these components was proved.

The new *Leptospermum* species is a shrub or small tree.

Oil of Limes. A notice[2]) concerning oil of limes distilled in Trinidad shows that the lime fruit products industry develops more and more in the West Indies[3]). Two samples tested in London showed the following properties: d 0.859 to 0.864, α_D + 43° and + 41°30′, $n_{D20°}$ 1.4740 and 1.4745.

This is the first time, we think, that there is a report on oil of limes from Trinidad.

H. Meaden[4]) writes on this industry in St. Lucia, regarding which we have said something on p. 33 of our *Report* of October 1918.

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[1]) *Journ. and Proceed. Royal Soc. of N. S. W.* **52** (1918), 175; *Perfum. Record* **10** (1919), 19. — [2]) *Perfum. Record* **9** (1918), 241. — [3]) Comp. *Report* October **1918**, 33. — [4]) *Bulletin of the Department of Agriculture*, Trinidad and Tobago **17**, 1, 4; *Perfum. Record* **9** (1918), 273.

Meaden visited the co-operative lime fruit products factory in St. Lucia, which was started in November 1913, at a cost of £ 550, for concentrating juice and distilling oil. In 1916—17, it was enlarged considerably, with the aid of a Government loan, and it is not at all unlikely that further extension will soon be required.

The cost of the Onderneeming factory, Demerara[1]), built in 1916, in its initial stage amounted to £ 645.

In this factory[2]) there are two stills, capable of containing 100 and 140 gallons of juice, respectively, both being coupled up to the same condenser. The juice in the stills is heated by steam, when the oil contained in it comes over with the steam into the condenser and is then collected in Florentine flasks.

The produce dealt with from May, 1915, to March, 1916, was 3029 barrels of fruit and 7122 gallons of juice, representing a total crop of 3920 barrels of fruit.

The limes are bought from the people or estate owners at a fixed price (3 s. 9 d. per barrel in 1917) and the juice at 6 d. per gallon.

Further details concerning the Government Lime Factory in Onderneeming, British Guiana, are found elsewhere[3]). In the fiscal year ending in March 1918, the factory bought 3504 bags of limes, yielding 27652 gallons of juice. Besides, 447 gallons of juice were bought. The total yield of oil amounted to 1100 lbs., *i. e.* 4 lbs. from every 100 gallons, against $3^1/_2$ lbs. during in the previous season. The yield from fresh juice on several occasions exceeded $4^1/_2$ lbs. per 100 gallons, while that from stale juice fell considerably.

Marsh rosemary Oil. Only a very few indications are to be found in text books, &c., regarding the essential oil of the marsh rosemary *(Ledum palustre*, L.; *Ericaceæ)*. We therefore welcomed the opportunity, we recently had, of distilling the oil ourselves. The sample of the herb that had been sent from Silesia, was rather small, it is true, but yielded a few grams of oil, so that we were able to determine the principal constituents. The yield from the faded herb amounted to 0.33 per cent. The properties of the distillate are widely different from the indications made hitherto concerning marsh rosemary oil[4]). It was lemon-yellow and its smell recalled somewhat that of coriander and wormseed oils: $d_{15°}$ 0.9189, α_D +4° 20′, $n_{D20°}$ 1.48451, acid v. 0.9, ester v. 27.0, soluble in 1 vol. and more of alcohol 90 per cent. No result was obtained, however, when trying to separate off ledum camphor by cooling the oil for some time to about —30°.

Oil of Monarda fistulosa. The oil of the North-American labiate *Monarda fistulosa*, L., has been investigated already by various authors[5]), recently by E. R. Miller[6]).

The oil distilled in 1915 was yellow or deep red, according to the time of the year in which it had been obtained: $d_{25°}$ 0.928, phenol content 58 per cent. The oil extracted from water showed the following properties: $d_{25°}$ 0.970, phenol content 98 per cent. The oil produced in 1916 showed $d_{25°}$ 0.9253, phenol content 57 per cent.; the oil from the distilling water: 0.972; n_D 1.5045; phenol content 96 per cent. In addition to the components discovered in the oil before; *viz.*, carvacrol, *p*-cymene, thymohydroquinone, thymoquinone and dihydroxythymoquinone, Miller proved the presence

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[1]) Comp. *Report* October **1918**, 33. — [2]) Apparently that in St. Lucia is meant. — [3]) *Perfum. Record* **9** (1918), 303. — [4]) Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd ed., vol. III, p. 409. — [5]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 465. — [6]) *Circular Univ. of Wisconsin No. 4*, October **1918**; *Chemist and Druggist* **91** (1919), 494.

of *d*- and *l*-α-pinene, two other terpenes not further identified, butyraldehyde, *iso*-valeraldehyde, piperonal (?), dihydrocuminic alcohol, another alcohol not further identified, acetic acid, butyric acid, valeric acid, capronic acid and basic bodies. The distilling water contained: acetone, formaldehyde, methyl alcohol, formic acid and acetic acid. The abstract does not give any clue as to how these bodies were identified.

Oil of Monarda punctata. An oil distilled in Montserrat from *Monarda punctata*, L., is described on p. 75 of this *Report*.

Mustard Oil. As it was difficult during the war to procure sufficient mustard powder for mustard plasters, so useful with children, A. Mertz[1]) has looked out for a suitable substitute, which he found in a mixture of 3 to 4 drops of mustard oil and 100 g. of *Bolus alba*. This preparation must be made very carefully, in order to avoid irritation. The paste to be applied is prepared by adding to above mixture about $^4/_5$ of its weight of boiling water and spreading the uniform paste upon the bandage. The success came up to the expectations and this substitute has the advantage over the natural product that it can be dosed exactly.

As to the physiological action of mustard oil, see page 112 of this *Report*.

Nutmeg Oil. The nutmeg market in Holland was greatly handicapped by the prohibition of exports and the lack of fresh arrivals; however, there was a good turn-over from second hand and for home consumption[2]).

The following quantities of cases were offered from first hand:—

Quality:	1914	1915	1916	1917
Stuktal, Banda, Siauw . . .	6077	5145	4182	683
id., accessory kinds . .	1152	495	1754	141
all kinds together	5616 (?)	5586 (?)	6499	1317

The prices, which owing to the prohibition of exports had risen to 165 cents, in November 1916, and then gone down to 82$^1/_2$, recovered gradually as far as 92$^1/_2$ and then suddenly rushed up to 194, in September 1917. Since then there was a general reserve and prices were rather steady at about 175 cents. The annual turn-over amounted to 13950 cases, against 30050, in 1916. Although official quotations have been stopped, in November 1916, it was still possible to make contracts in Amsterdam.

Oil of Ocimum gratissimum. The oil of *Ocimum gratissimum*, L. *(Labiatæ)*, obtained on the Ivory Coast and in Central Africa, distinguishes itself by its high content of thymol and strongly resembles ajowan oil in smell[3]). It is remarkable that the oil distilled from the same plant in Mahé (Seychelles) has different properties and a different composition[4]).

Ocimum gratissimum grows in Mahé as a weed. The distillation of the entire plant yielded 0.1 per cent. of a light-brown oil with a pronounced clove odour and a peculiar, not very agreeable accessory smell. d_{15° 0.995; α_D — 14.1°; n_{D21° 1.526; sol. in 0.7 vol. of alcohol 80 per cent. It contains 62 per cent. of phenols, in the main eugenol.

The oil has but little value for perfumery and, on account of the scanty yield, could hardly be used to advantage for the manufacture of eugenol.

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[1]) *Deutsche med. Wochenschrift* **1919**, no. 17; *Pharm. Ztg.* **64** (1919), 359. — [2]) *Wirtschaftsdienst* **1918**, 889. — [3]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 580. — [4]) *Bull. Imp. Inst.* **16** (1918), 32, *Journ. Soc. chem. Industry* **37** (1918) A. 604. It is not indicated, however, who gave the plant that name.

Palmarosa Oil. We discussed at the time an article by R. S. Pearson[1]) on the *Rosha* oil industry in British India, mentioning that the author thought it possible to raise the annual production from about 150000 to 225000 lbs. by introducing the steam distillation, but that it was doubtful, whether the market could take up such a quantity without there being a considerable fall in price.

Trials have now been made on a small scale, in the Melghat Division, in order to obtain palmarosa or gingergrass oil by steam distillation. So far, nothing is known about the results[2]).

Patchouly Oil. G. L. Logan[3]) has published a short notice on the production of patchouly oil in the Straits Settlements, from which we copy the following particulars:— The patchouly plant *(Pogostemon Patchouli,* Pell.; *Labiatæ)* is often planted by the Chinese in places where the forest has been recently cleared. A little shaded, it grows there fairly quickly and luxuriantly between the trunks of the felled trees. Where it is really cultivated, it is planted on properly prepared beds. It is best propagated by slips from young shoots. They must be about 7.5 cm. long and cut just underneath a knot. They are put in frames, well watered and shaded. After 3 or 4 weeks, they have formed roots, so that they can be transplanted to the proper beds, where they must be shaded till they have rooted. It is true, the plant can be cultivated too in the sun, but a little shadow is advantageous. The distance between the slips is about 2 feet.

The first crop takes place six months after planting and is then repeated twice yearly. In Perah, the plantations are renewed after three crops.

Spread out in the shadow, the leaves get dry in about a week's time. A picul (133 1/2 lbs.) of leaves dried immediately after having been gathered, yielded from 24 to 39 ozs. of essential oil; a sample without stalks, about double the quantity. From 1/20 acre, 449 lbs. of green herb were gathered, corresponding to 106 lbs. of dry material, which yielded 69 lbs. of good leaves and 37 lbs. of refuse.

The dry patchouly leaves are exported principally to Marseilles and New York. In 1916, nearly all the exports of Penang went to New York, the quantity being 65 tons. In 1917, the total exports of patchouly leaves from Penang to the United States amounted to 79979 lbs. to the value of $ 12252 gold.

As to patchouly-growing in the Dutch East Indies, see p. 82 of this *Report.*

Pennyroyal Oil. Oil of pennyroyal (from *Hedeoma pulegioides* [L.], Pers.; *Labiatæ*) is one of the few oils containing pulegone. According to Barrowcliff's latest investigation[4]), the oil contains, in addition to pulegone, *1*-methyl-*3*-cyclohexanone, *1*-menthone and d-*iso*menthone. If therefore 80 to 90 per cent. of "pulegone" are found by the sulphite method, this figure refers to the mixture of ketones mentioned, as C. T. Bennett[5]) points out.

The pennyroyal ketones are absorbed far more slowly by the sulphite than those of other essential oils, such as caraway and dill oils, and shaking must be continued for about three hours, as otherwise the figures arrived at would be too low. In one instance, the ketone content found was 44 per cent. after one hour's shaking with the sulphite solution, 58 per cent. after the second hour and 88 per cent. after three hours.

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[1]) *The Indian Trade Journal; Indische Mercuur* **39** (1918), 787; *Report* October **1917**, 31. — [2]) *Perfum. Record* **9** (1918), 208. — [3]) *Commerce Reports* of September 1918, *Americ. Journ. Pharm.* **90** (1918), 733. — [4]) Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 467. — [5]) *Perfum. Record* **9** (1918), 208.

Pepper Oil. The pepper trade in the Dutch Indies kept in prosperous condition, in 1917[1]), owing to American purchases. The Lampong crop is estimated at 170000 tons, as compared with 120000 in the previous year. The exports amounted to 12239 tons against 9338 in 1916. Prices for black pepper oscillated between 34 and 53 florins per picul.

The Lampong and Muntok crop is said to have been good in every respect, regarding that of 1917/18, nothing accurate is known so far.

Amsterdam had been without arrivals for a long time, so that business was very quiet and, as exports were prohibited, was restricted to second hand for home consumption. White Muntok, quoted for at 85 cents, in the beginning of 1917, rose to 215 towards the end of the year, black Lampong, from 50 to 75.

Peppermint Oil, American. This year's crop is reported to have yielded only about 260000 lbs., of which 80000 lbs. are in the hands of well-to-do producers, who do not mean to sell in the expectation of higher prices. Crude oil was quoted for, in the beginning of September, on the New York market at $ 7.50 per lb. and no decline is expected. On the contrary, higher prices are prognosticated for the future, reaching perhaps $ 10.— per lb. Such a high price might prove prohibitive for the German buyer.

Peppermint Oil, Dutch. From two parcels of dry peppermint herb, grown on the island of Walcheren, oils of the following properties were distilled in Holland[2]), the yield being 0.7 and 0.95 per cent., respectively: $d_{15°}$ 0.907 and 0.906, α_D —29.2 and —29°, $n_{D29°}$ 1.4621 and 1.4615, acid v. 0, ester v. 23.7 and 21, ester v. after acetylation 194.3 and 188, ester menthol 6.7 and 5.9 per cent., total menthol 63.4 and 61 per cent., soluble in 4½ and 3½ vols. of alcohol 70 per cent. and in ¼ vol. of alcohol 90 per cent.

After the rectification, the figures were as follows: $d_{15°}$ 0.907 and 0.905, α_D — 29.2 and 29.1, $n_{D20°}$ 1.4619 and 1.4610, acid v. 0, ester v. 22.9 and 22.8, ester menthol 6.5 per cent., total menthol 66.4 and 63.3 per cent., soluble in 3 vols. of alcohol 70 per cent. or in ¼ vol. of alcohol 90 per cent.

There is nothing very favourable to report on the peppermint oil trade during the last year. Scarcely any of the samples submitted to us for testing were faultless, but most of them more or less grossly adulterated. The lack of fresh arrivals and the vivid demand led many a supplier to "stretch" their stocks, the climax being reached by a certain Leipzig firm, whose dishonourable methods we have repeatedly had to mention in this *Report* (comp. pages 15, 63, 68). First of all, it had operated with phthalic ester, in some instances to an almost incredible extent, the percentages being 55 in one case and 65 in four others, so that one might almost have spoken of phthalic ester perfumed with peppermint oil. Not only a considerable amount of cheek, but also a great trust in the credulity of the buyers is required for daring to sell such stuff. In the latter respect, the firm had miscalculated, however, and we had a chance to prevent customers from being taken in. It was not a matter of trifles, for in one such case the invoice value was 130000 Marks, of which said firm struck at once 110000 (one hundred and ten thousand) Marks after the adulteration had been disclosed through our analysis! This shows what the profits of this cheating must be, if it is not possible to reveal it in time.

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[1]) *Wirtschaftsdienst* **1918**, 888. — [2]) *Pharm. Weekblad* **56** (1919), 41.

As many consumers may be interested perhaps in particulars, we beg to indicate the constants of such faked oils, together with the figures for a good pharmacopœia quality, for comparison's sake: —

	1.	2.	3.	4.	5.	pharmacopœia
$d_{15°}$	1.0217	1.0597	1.0521	1.0588	1.0663	0.900 to 0.910
α_D	— 12° 46′	— 8° 30′	— 7° 25′	— 8°	— 7° 7′	— 25 to — 30°
solubility in 70 per cent. alcohol	1.8 vol.	—	1.3 vol.	1.3 vol.	1.5 vol.	2 to 4 vol.
acid v.	1.9	—	0.6	0.6	0.3	up to 1.8
ester v.	315.5	389.2	373.2	385.6	400.5	abt. 8 to 34
ester v. after acetylation	357.5	412.5	—	—	412	not under 158
acid v. II (comp. *Report* Oct. **1910**, 63)	—	12.1	—	—	—	= sap. v.
difference between sap. v. and acid v. II	—	377.1	—	—	—	0
contents of phthalic ester	abt. 55 p.c.	abt. 65 p.c.	abt. 65 p.c.	abt. 66 p.c.	abt. 69 p.c.	—

A comparison shows that all the oils adulterated with phthalic ester are conspicuous by their high specific gravity, their low rotation and, above all, by their abnormal ester value. The latter constant deserves the greatest attention of the analyst, for even if it does not exceed the normal figures to such an extent as in the present case, the suspicion of an adulteration is given.

The acetylation value does not, of course, afford any clue as to the quantity of total menthol, as it depends in the main upon the phthalic ester and is, in consequence, far too high. For instance, the acetylation number of 357.5 indicated under 1, would correspond to a menthol content of 136 per cent., *i. e.* quite an impossible figure.

The content of phthalic ester mentioned in the foregoing tables has been calculated mostly from the ester value of the oils. It is to be ascertained more precisely from the difference between the saponification value and the acid value II, for it discloses direct the quantity of the phthalic acid present. In this way, the value for oil no. 2 has been determined. The phthalic acid was separated in the usual way and characterized by its m. p. (195 to 197°) or that of its anhydride, obtained through sublimation (130°).

The firm in question has shown a certain ingenuity in faking peppermint oils. Of two other such oils from the same source, one was adulterated with glycerol acetate, the other with alcohol. The former behaved as follows: $d_{15°}$ 0.9144, α_D — 29° 37′, acid v. 03, ester v. 93.3, incompletely soluble in 10 vols. of alcohol 70 per cent., soluble in 1 vol. and more of alcohol 80 per cent., dilute solution opalescent. The high ester v. led to suspecting the presence of artificial ester, the nature of which was disclosed on shaking the oil with water and evaporating the aqueous solution on a water-bath. A residue of the high ester v. 686.5 remained, which in addition to the solubility in water pointed to glycerol acetate. In accordance with this, the specific gravity of the oil was much lower after the shaking with water than before. A quantitative determination (comp. *Report* April **1911**, 150) showed that about 10 per cent. of glycerol ester were present. Taking into consideration the ready solubility of said ester, the insufficient solubility of the oil clearly shows of what inferior quality it must have been.

The oil adulterated with alcohol made itself suspicious by its very low specific gravity, whereas the other constants were normal: $d_{15°}$ 9.8825, α_D — 19° 35′, acid v. 0.45, ester v. 48.0, ester v. after acetylation 198.3. Our supposition that the oil had been adulterated with alcohol proved correct and it resulted that the quantity added amounted to nearly 30 per cent., which showed again that the firm in question is not satisfied with trifles. This peppermint oil had expressly been denominated "pure, concentrated!"

It would lead too far to enumerate all the adulterated peppermint oils we have had to test. We only add, therefore, that we have had before us a considerable

number of samples of adulterated oils and that glycerol acetate and phthalic ester took the first place under the admixtures. Generally speaking, the quantities added were more modest than with the firm referred to.

However, we cannot refrain from mentioning another sample, which was so to speak the acme of the art of "composing". It had the following constants: $d_{15°}$ 0.9459, α_D — 20°43', soluble in 2 vol. and more of alcohol 70 per cent., acid v. 0.7, ester v. 64.4, ester v. after acetylation 231.3, acid v. II 12.1, difference between saponification v. and acid v. II 53. The very high specific gravity rouses suspicion above all, as it cannot be explained by resinification, for a resinified oil is characterized by insufficient solubility, whereas the sample under examination was specially well soluble. Furthermore, the high acetylation v. attracts attention, as it would correspond to a content of 77.9 per cent. of total menthol, *i. e.* a quantity found only in the normal, unseparated Japanese peppermint oil. The difference between the saponification v. and the acid v. II confirmed that the oil was adulterated. As contrasted with pure peppermint oil (see tables on page 39), the difference is here 53, which shows that the oil contained the ester of a non-volatile acid. The acid proved to be identical with phthalic acid and was recognized for instance by its m. p. of 195 to 196°. It was present, without doubt, in the form of phthalic ester, the quantity of which could be calculated at about 10 per cent. from the difference mentioned.

But this was not the only adulteration, for a closer investigation revealed the presence of anethole and of characteristic sandalwood oil components. It is even possible that the product did not contain any peppermint oil at all, but was a mixture of other substances, to which some menthol had been added. Under the circumstances, the acetylation v. does not give any clue as to the content of total menthol, but this is a minor detail with such stuff.

The value of mint as fodder. Like other industries, that of the essential oils tries to make the best use of its by-products. In isolated cases, as for instance with certain seeds, the distillation residues are used as fodder for cattle, but most of such materials have but little practical value. Distilled peppermint herb is said to be an appropriate fodder for animals and in this respect an article by O. Dafert[1]), entitled "The Value of Mint as Fodder" is of interest for us. He examined the chemical components of the herb of the ordinary and of the Japanese peppermints, before and after the distillation. For the residues of distillation of the former, he found the following composition: water 7.55 per cent., crude proteine 18.81 per cent., fat 1.64 per cent., extractive matter free from nitrogen 49.85 per cent., crude fibre 8.69 per cent., ashes 13.06 per cent. (sand 1.4 per cent.) The residues of the Japanese mint contained a little less crude proteine and a little more crude fibre, but otherwise resembled those of the ordinary peppermint. The values ascertained almost equal those of dry leaves, so that these residues of distillation would have about the same value. The quantity of such residues can be estimated at from 16 to 24 cwts. per hectare, under favourable conditions even at 40 cwts.

It might be of interest to ascertain whether such residues have any effect on the digestion and the state of health of the animals, as there do not seem to be any particulars on this subject given in the competent text books.

One of the best-known pests is the peppermint rust (*Puccinia Menthæ*, Pers.), which often occurs in summer and autumn even on our wild mints and forms orange-coloured

[1]) *Zeitschr. f. d. landw. Versuchswesen in Österreich* **17** (1914), 839; *Heil- u. Gewürzpflanzen* **2** (1918), 65.

bolsters on them. The persistent summer rain in 1913 (1918?) has, as B. Grof[1]) reports, favoured the development of this fungus pest on the wild as well as on the cultivated varieties of mint. He describes the pest on the Japanese peppermint *(Mentha canadensis*, var. *piperascens)* as follows: The aecidium appears at the end of April on the stalks of the shoots of from 10 to 12 cm. in length, causing swellings. The lower leaves dry up, whereas the upper ones remain green. The uredospores appear in July, the teleutospores at the end of September. A severe attack may bring about a complete failure of the crop and impairs the quality of the oil. In order to destroy the fungi, the leaves that have fallen off are collected in autumn and burnt. The beds attacked are sprayed with a 2 per cent. copper sulphate solution, which is repeated in spring, and the mint is then cut in June, before the uredospores appear.

Peppermint Oil, French. D. Coste[2]) reports on the cultivation of peppermint in the Basses-Alpes, in an article from which we extract only the following particulars. Peppermint plants may reach a height of 75 to 90 cm. in good soil, when the yield may amount to 15000 to 20000 kilos per hectare, whereas on inferior soil it would be 10000 to 15000 kilos of fresh herb. The value of the fresh herb, as bought by the distillers, is 1500 to 2000 Francs per hectare, for good soil. The maximum yield would be 2 kilos of oil from 1000 kilos of fresh herb.

In 1910, peppermint was grown on an area of about 10 hectares in the neighbourhood of Castellane.

Peppermint Oil, Japanese. In the last weeks, the Japanese market showed a tendency to adapt itself to the American conditions, so that a considerable rise resulted, the more so as the bad crop will force the United States to import more Japanese oil than in previous years for stretching the stocks at home. There is a firm tendency in London as well and considerably higher prices are to be expected during the winter. The unfavourable rates of exchange will have their share too in raising the price of the pharmacopœia quality, which is manufactured from Japanese oil.

The exports from Japan during the first six months were as follows[3]): —

	1917	1918	1919
kin	106232	78603	198724
to the value of yen . .	235784	161671	530649.

A few years ago, it was tried successfully to introduce into Germany and the German colonies slips of Japanese peppermint; in Dahlem they developed excellently and yielded an oil rich in menthol[4]). The United States have been less fortunate in this respect[5]), as they have repeatedly tried in vain to import living Japanese peppermint plants. Only once, a consignment had arrived in good condition, owing to special precautions, but unfortunately the sanitary authorities went so far in their zeal as to disinfect the plants thoroughly, in consequence of which not a single one survived.

According to the American Commerce Reports, it has been tried, in Japan, to obtain seeds from the Japanese peppermint plant (Black Mint), but without success so far.

This plant is cultivated, in Japan, in two regions of different climatical character. The lion's share of 92 per cent. belongs to Hokkaido (Jesso), the large northern island,

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[1]) *Heil- u. Gewürzpflanzen* **2** (1918), 66. As per a discussion in the *„Internationale agrartechnische Rundschau"* (original Hungarian). — [2]) *Parfum. moderne* **11** (1918), 137. — [3]) *Chemist and Druggist* **91** (1919), 1105. — [4]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 503. — [5]) *Perfum. Record* **9** (1918), 242.

where the average temperature during the winter is about — 5.5, the lowest about — 23°, the average summer temperature about 15.5, the maximum about 32° and the average annual rainfall about 95 cm. The remaining 8 per cent. are grown in the prefectures of Okayama and Hiroshima on the main island, where the corresponding figures are as follows: average winter temperature about 3.5, minimum about — 6.5, average summer temperature about 24.5, maximum about 36.5° and the average annual rainfall about 196.5 cm. The largest part of the Black Mint is therefore cultivated, in Japan, under climatical conditions equalling those of Virginia or North Carolina.

Pine-needle Oils. In an article by L. E. Andés[1]) on essential oils obtained from the needles of spruce-firs, pines, etc., there are some notes on the production of oil from the needles of the black-pine, tried in Austria during the war, but which proved absolutely unremunerative, owing to the extremely scanty yield.

At the end of the article, the author points out that in our (the Austrian are here surely alluded to) forest laws, there was not sufficient stress laid upon the fact that the production of resin as well as the accessory industries, such as the distillation of oil from needles, cones, etc., constitute a great danger for the woods. On the one hand, the trees are handicapped in their growth, thus producing less timber; on the other hand, the workers would trample down the undergrowth and increase the risk of fire. As, however, the the views on this subject seem to have changed, owing to the scarcity of turpentine and allied products, so that even competent quarters speak in favour of an extensive production of resin, Andés thinks that there is not much to be said either against depriving the conifers of a moderate member of their needles.

Following up the little notes, which we have published occasionally on the fatty oil of fir-seed[2]), we wish to acquaint our readers with an article by R. Francé[3]), which appeared in *"St. Hubertus"*. He has found that fir-needles contain an oil which might easily be used for technical purposes on account of being completely saponifiable. The more the warm season advances, the scarcer it gets, whereas it is present in a greater proportion during cold periods. As stated by him, it can be obtained too from needles that have recently fallen. The oil resists the same temperature as the tree itself.

It seems from this notice that a fatty oil is referred to.

Oil of Pycnanthemum lanceolatum. The labiate *Pycnanthemum lanceolatum*, Pursh., growing in the United States, contains an oil, which it is difficult to distinguish in smell from pennyroyal oil and which, according to Corell[4]), contains carvacrol and pulegone. E. R. Miller[5]) confirms the presence of these two bodies and indicates as further constituents: geraniol, dipentene, most likely two other terpenes and perhaps also thuyone. The young plants contain less ketones than the older ones. After reaching a maximum, however, the amount of the ketones diminishes as the age of the plant advances. Young plants give as much carvacrol as more fully developed specimens. The percentage was found to vary from 14.5 to 58 per cent., the majority of the oils having 25 per cent. or more. The amount of ketones varies between

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[1]) *Deutsche Parf.-Ztg.* **5** (1919), 45. — [2]) Comp. for instance *Report* October **1917**, 41. — [3]) *Zeitschr. f. angew. Chemie* **31** (1918), III. 490. — [4]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III. p. 490. — [5]) *Circular, Pharm. Exper. Stat. Univers., Wisc.* **2** (1918); *Chem. Abstracts* **12** (1918), 1410. According to *Perfum. Record* **9** (1918), 256.

3 and 40 per cent. One sample only was tested quantitatively for terpenes, it gave about 20 per cent.

It is not mentioned in the discussion, in which way Miller identified the various constituents.

Rose Oil, Anatolian. It was reported in summer 1918 that the prospects for the 1918 rose crop in Anatolia were very unfavourable, as in the principal districts (Sparta, Vilajet Aidin, &c.) the fields were used in the main for growing cereals or, in part, left uncultivated altogether[1]). The reason for not cultivating roses was, in addition to the scarcity of hands, the fact that the wood required as fuel for the distillation can only be had at exorbitant prices. This year's production is estimated at about 50 to 60000 miscals (1 miscal = 1.5 dram). Rose oil is no longer an article of commerce properly speaking, but, owing to its high price and its being easily handled, a favorite investment or object of speculation. There is scarcely any real market price at present, but what is paid cannot be called excessive, if compared with the prices before the war. From one source 75 piastres per miscal (about ℳ 3100.— per kilo) is named, whereas another firm quotes ℳ 2600.— per kilo. The inconsiderable rise is due to the fact that the Turkish export regulations hardly permit of a regular export.

Rose Oil, Bulgarian. According to a report[2]), received by the German Balkan Society, from Kezanlyk, the 1918 production is far behind that of the previous year, presumably by 25 per cent. Strong frost in March and the drought during the time of distilling are responsible for the shortage. As the quality of the flowers was inferior too to last year's, 24 kg. of petals were required for producing 5 g. of otto of roses, as compared with 15 to 16 kg. in the year before. Although the prices have not been fixed definitely as yet, it is to be expected that they will exceed last year's by about 40 to 50 per cent. This rise is explained not only by the conditions mentioned before, but is due also to higher wages, higher cost of fuel for distilling, &c., and to the fact that the peasants demand very high prices for their produce. Rose petals cost 60 stotinki per kilo, this year.

The 1919 crop is said to have yielded barely 1500 kg. of oil, being therefore the smallest for many years. As per the communications from our informant, the prospects for next year seem to be very unfavourable, as very little attention and care has been bestowed on the rose fields. Owing to the fabulous prices obtained during the war for cereals and leguminous fruits, agriculture has developed only in this direction, all the more so as the cost of labour, fuel and living has risen tremendously in the rose districts. Nevertheless, the rise in the prices of rose oil might have kept within reasonable limits, if the Government had not suddenly commandeered all the stocks in the hands of producers, dealers and banks, which measure sent the prices up by leaps and bounds to the equivalent of about ℳ 10000.—. This step of the Government was necessary in order to secure an article of compensation for the food supplies which America was ready to send. It is safe, in consequence, to presume that the lion's share of this year's production has been shipped to the United States and that present stocks are reduced to what was stored abroad and hence escaped commandeering.

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[1]) *Nachr. f. Hand., Ind. u. Landw.* **1918**, No. 161, p. 9. — [2]) *Deutsche Levante-Ztg.* 8 (1918), 474.

The New York Oil, Paint and Drug Reporter[1]) publishes the following particulars concerning what happened in May:

By an agreement between the Bulgarian Government and the United States Food Administration (Grain Corporation), the starving Bulgarian populace will be supplied with American articles of food, which will be paid for with the proceeds of otto of roses, the only product Bulgaria has at her disposal for export to this country. The total quantity has been shipped already to America and is under the joint control of the U. S. Food Administration and a Bulgarian official, called L. Getschcoff. On June 4th, negotiations took place with the principal Bulgarian rose oil merchants regarding the distribution and an agreement was arrived at, according to which the 1919 product is not to be sold under $ 17.50 per oz., contrary to Mr. Getschcoff's expectations, who had asked for more. Generally speaking, the American consumers refuse to pay this fabulous price and have availed themselves very little of the stocks. It is not known what quantity the U. S. Government holds for account of the Bulgarians, but it is supposed to be considerable. Bulgaria was willing to pay the foodstuffs in gold, but the United States demanded goods. In consequence, the Bulgarians raised their prices at once, in order to get rid of their debts quickly. It would be interesting to know how much adulterated oil the U. S. Government accepted in these purchases.

Otto of roses being so valuable just now, adulterations are highly remunerative, especially if practised to such an extent as was the case with a sample submitted to us for testing. The admixture, consisting of palmarosa oil most likely, amounted to 20 or 30 per cent., as could be inferred from the geraniol content, which was 79.4 per cent., whereas it never exceeds 75 per cent. with a normal otto of roses. Besides, the adulteration had raised the specific gravity, the refraction and the ester value, but lowered the point of solidification. Rotation and acid value were normal: $d_{30°}$ 0.8659, α_D —1° 50′, $n_{D25°}$ 1.46628, solidification point +15.4°, acid v. 0.5, ester v. 19.3.

Another oil was apparently adulderated in a simliar way, only that it had been done more artfully. It had been tried to balance the lowering of the solidification point, caused by the palmarosa oil, by adding spermaceti, but the dose had been exaggerated. Hence the oil solidified at 28°, as compared with 18 to 23.5° for the normal commercial quality. The stearoptene isolated from it distinguished itself considerably in melting point and saponification from pure rose oil stearoptene. Whereas this melts at about 35° and has a saponification number of from 3 to 7, the stearoptene of the oil in question melted between 49 and 51° and showed a saponification value of 123.2, which proved that it consisted in the main of spermaceti (m. p. 45 to 54°, sap. v. 128 to 130).

This result was sufficient to confirm that the oil had been grossly adulterated, so that we thought it superfluous to go further into the chemical examination, only establishing the physical properties: $d_{35°}$ 0,8619, α_D —1° 26′, $n_{D35°}$ 1.46971. The excessive specific gravity, which corresponds to 0.8656 at 30°, calls special attention, all the more so, as the elevated solidification point would lead to expect a light oil. This contradiction is explained, however, by the above statements.

Rose Oil from Cyprus. Only quite occasionally notes have appeared on the production of otto of roses in Cyprus, among which an article was published quite

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[1]) *Chemist and Druggist* **91** (1919), 723.

recently in an English periodical[1]). In spring 1917 and 1918, a small quantity of excellent quality has been distilled there. That obtained in 1917 was a golden yellow, semi-congealed mass, possessing the characteristic intense odour of otto of roses. The constants were found to agree closely with those recorded for Bulgarian rose oil. According to experts, Cyprus otto of roses has a fairly good but somewhat weak odour.

In 1918, the oil was distilled between the 7th and 23rd May. The distillation was carried out in two different ways: on the one hand distillation of roses together with buds, sepals and peduncles, on the other, with petals only. According to the first method, 944 okes of material yielded 92 drams of oil, *i. e.* 10 okes 104 drams of material for every dram of oil, as against 8 okes 250 drams to one dram of oil in 1917. The difference was due to the rainy weather in the first weak of distillation, in 1918. In the second way only 50 okes of roses were used, yielding 13 okes 100 drams of petals, from which just one dram of rose oil was obtained. Distillation was carried out with native "souma" stills in a proportion of 3 okes of water to 1 oke of roses, from which 1 oke of rose water was obtained for every oke of roses. This rose water was redistilled, and one third of the quantity of the original rose water was then obtained. This was placed in 2½ oke bottles, kept submerged in cold water for 24 hours, when the floating oil was collected by means of a pipette.

Sandalwood Oil, East Indian. In December 1917, the Committee of the Upper India Chamber of Commerce had to occupy itself with a memorandum handed to the Government by the perfume manufacturers of Kanauj, containing a protest against the Mysore Government's decree, prohibiting all sales by auction of sandalwood for the manufacture of oil and claiming it all to be reserved for the Government factory at Bangalore[2]). According to said memorandum, it was to be feared that the Madras Government would have to reserve for Mysore all the Coorg and Coimbatore sandalwood. After having examined the matter, experts have advised the Committee not to grant the petition, as in Kanauj the sandalwood oil is not distilled in an economical manner. The perfumers might buy oil from Mysore and wood from Coorg and Coimbatore. In any case, internal matters of the state could not be interfered with. The Committee, therefore, decided not to do anything in the matter.

The Department of Statistics publishes the following figures regarding the transmarine exports to foreign countries for some months of 1918[3]):—

Exports from:	Bombay		Madras		Bengal	
March	35 galls.	5550 Rs.	13 galls.	3950 Rs.	— galls.	— Rs.
April	528 „	132000 „	— „	— „	640 „	108475 „
May	408 „	102000 „	— „	— „	33 „	7013 „
June	11 „	3360 „	— „	— „	119 „	36000 „
July	1248 „	312032 „	— „	— „	778 „	217456 „
August	1887 „	451050 „	213 „	57660 „	100 „	30540 „
September	979 „	249279 „	— „	— „	9 „	2160 „

Some time ago, a seemingly more rational method has been adopted for the manufacture of sandalwood oil in British India[4]). This is confirmed by a notice in a periodical[5]), according to which the Bangalore factory produced 59690 lbs. of oil in the year 1916/1917. After £ 55425 had been paid to the Forest Authorities for

[1]) Perfum. Record **10** (1919), 29, 140. — [2]) Comp. *Report* April/October **1918**, 44. — [3]) Perfum. Record **9** (1918), 207, 270; **10** (1919), 14. — [4]) Comp. *Report* October **1918**, 43. — [5]) *Der neue Orient* **3** (1918), 499.

the wood, there was a net profit of £ 32641. At present, a second factory is being built at a cost of £ 19466. As per the experience gathered so far, the distillation pays and there is an active demand for the oil in the London market. Two experts have been engaged, who test the oil before it is shipped.

We have reported repeatedly of late on the adulteration of sandalwood oil with benzyl alcohol[1]). Although benzyl alcohol has become scarce meanwhile, it is still being used for said purpose, as was shown by a sample we had an opportunity to test in the course of this year. We would call special attention to this case of adulteration, as it had been carried out with great ability, so that the constants were quite normal: $d_{15°}$ 0.9799, α_D — 16° 46′, acid v. 3.7, ester v. 7.5, ester v. after acetylation 200.0, soluble in 4,5 to 5 vols. of alcohol 70 per cent. Distillation first showed that the article was not pure, for on boiling in a Ladenburg flask about 10 per cent. passed over between 210 and 280°, whereas a pure oil, treated in the same way for the sake of comparison, only just started to boil above 280°. The low-boiling fraction contained benzyl alcohol, as was proved on closer investigation, which had been added without doubt in order to "raise" the santalol content, as 1 part of benzyl alcohol foreshadows a little more than two parts of santalol. The acetylation v. indicated is not, under the circumstances, a criterion for the real santalol content.

In a decree of 19. 2. 19, no. 2781, the Austrian Department of Public Health warns against using West Indian sandalwood oil in lieu of the East Indian variety[2]). It had been found that sandalwood oil capsules, in consequence of the scarcity of the official article, had been filled with the West Indian oil, which does not come from a *Santalacea*, but from a *Rutacea (Amyris balsamifera)*. Said authority considers this to be not only a falsification but also a dangerous proceeding, as the so-called West Indian sandalwood oil contains a far higher percentage of irritating terpenes than the East Indian quality.

Savin Oil. It is a well-known fact that oil of savin causes abortion. Even if taken in fairly small quantities, it may produce fatal effects. A. Welcker[3]) reports on a deadly case of poisoning *(Abortus criminalis)*, when a woman 32 years old took two doses of 5 grams each, on two consecutive days in the sixth week of pregnancy. The effect was miscarriage, uræmia and death.

Spearmint Oil. The article has been very scarce in Germany for many years and for small quantities of a very doubtful quality prices were exacted that seem unbelievable. In the United States, the stocks from last years crop seem to have been cleared and according to the available reports the yield of this year's crop is estimated at 13000 lbs., whereas the total consumption is said to be about 50000 lbs. The price was about $ 10.25 lbs. in the beginning of September and a rise was expected. Under these circumstances, the article will most likely disappear altogether from the European market.

F. Rabak[4]) studied, some years ago, the influence of cultivation and climate on the yield and the properties of peppermint oil. He has now done the same with regard

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[1]) Comp. *Reports* October **1913**, 98; October **1916**, 49; April/October **1917**, 58. — [2]) *Zeitschr. d. allg. Österr. Apoth. Ver.* **57** (1919), 60. — [3]) Nederl. Tijdschr. v. Geneesk. **1918**, II. 1307; Therap. Monatsh. **33** (1919), 158. — [4]) *U. S. Dep. Agric. Bull.* No. 454, Washington 1916; *Report* October **1917**, 35.

to spearmint. The results of his investigations are contained in an article called: "Influence of time of harvest, drying and freezing of spearmint upon the yield and odorous constituents of the oil."

The cultivation of spearmint is conducted extensively in the United States for the production of the volatile oil, which is used largely for the flavouring of chewing gum.

Rabak grew the spearmint plants at Arlington Farm, Va., and his investigations extended over the years 1908, 1909, 1910 and 1911. The plants were gathered at three distinct stages of growth; viz., budding, flowering and fruiting stages. They were distilled in both fresh and dried conditions and the oils subjected to examination and compared both as regards yield of oil and physical and chemical composition. At the same time, the leaves and flowering tops were separated from the fresh material at the different stages of growth and distilled in order to obtain information regarding the distribution of the oil in the plant and composition of the oil from the plant parts as compared with the whole fresh herb.

Rabak found that the yields apparently vary with the season. In 1908 and 1911, they were considerably higher than in 1909 and 1910. The yield of oil from the fruiting plant was low, while the flowering stage produced the highest yield. Dry herb always yielded less oil than the fresh plants. The average percentage of moisture during the years 1909, 1910 and 1911 was as follows: Budding stage, 71.6; flowering stage, 70.7; fruiting stage 62.2 per cent.

Yield of oil from the fresh and from the dry spearmint herb at different stages of growth during the years 1908 to 1911:

Fresh herb,	budding	0.11	to	0.30,	on an	average	0.187	per	cent.,
„	„ flowering	0.15	„	0.26,	„	„	0.205	„	„ ,
„	„ fruiting	0.07	„	0.24,	„	„	0.127	„	„ ,
dry	„ budding	0.083	„	0.15,	„	„	0.124	„	„ ,
„	„ flowering	0.097	„	0.22,	„	„	0.142	„	„ ,
„	„ fruiting	0.037	„	0.14,	„	„	0.084	„	„ .

The yield from the whole herb is generally lower than that from either the leaves or flowering tops, due to the presence of stems. The flowering tops yielded uniformly more oil than the leaves. (The tops during the fruiting stage show the highest oil content.)

Yield of oil from the fresh herb, leaves and tops spearmint at different stages of growth:

a) Whole herb:

budding stage	0.11	to	0.23,	on an	average	0.15	per	cent.,
flowering „	0.15	„	0.26,	„	„	0.2	„	„ ,
fruiting „	0.07	„	0.24,	„	„	0.173	„	„ ;

b) Leaves:

budding stage	0.08	to	0.24,	on an	average	0.176	per	cent.,
flowering „	0.20	„	0.25,	„	„	0.223	„	„ ,
fruiting „	0.05	„	0.41,	„	„	0.203	„	„ ;

c) Tops:

budding stage	0.08	to	0.42,	on an	average	0.260	per	cent.,
flowering „	0.14	„	0.48,	„	„	0.310	„	„ ,
fruiting „	0.05	„	0.41,	„	„	0.243	„	„ .

The physical and chemical properties of the various oils determined by Rabak were colour, odour, taste, specific gravity, rotation, refraction, solubility in 80 per cent. alcohol, acid value, ester value (calculated as acetate of the alcohol $C_{10}H_{18}O$) and alcohol content calculated as $C_{10}H_{18}O$.

The most fragrant oil was yielded by the fruiting plants. As to colour, specific gravity and refraction, Rabak did not notice any regularity. The rotations of the oils were comparable during any one season but differed from season to season, while the solubilities varied likewise. The solubility of the oils from the flowering and the fruiting stages excelled that of the budding herb, which would perhaps indicate a higher content of esters and alcohols, and a lower content of terpenic compounds in the former. Generally speaking, the odour of oils from the dry herb was more agreeable than that of oils from the fresh plant, although accompanied by a herb-like smell. Specific gravity, rotation and refraction averaged lower in case of the oils from dry plants than those from the fresh herb and they were distinctly more soluble in 80 per cent. alcohol. The ester content varied and was highest in the oils from the flowering and the fruiting dry herb. The formation of esters and alcohols seemed to be favoured by the drying process.

Physical and chemical properties of spearmint oils from various parts of the plant at various stages of growth.

A. Whole plant, budding stage:

$d_{21°}$ 0.9316 and $d_{23°}$ 0.9312; α_D — 32.6 and — 45.6°; $n_{D21°}$ 1.4891 and $n_{D23°}$ 1.4895; acid v. (calculated as acetic acid) 0.32 and 0.14 per cent.; ester v. (calculated as acetate of $C_{10}H_{18}O$) 8.6 and 7.6 per cent.; alcohol content (calculated as $C_{10}H_{18}O$) 12.0 and 16.0 per cent.

B. Whole plant, flowering stage:

$d_{21°}$ 0.9289 and $d_{24°}$ 0.9252; α_D — 32.2 and — 40.6°; $n_{D21°}$ 1.4864 and $n_{D24°}$ 1.4825; acid v. 0.26 and 0.69 per cent.; ester v. 7.7 and 13.4 per cent.; alcohol content 12.4 and 17.0 per cent.

C. Whole plant, fruiting stage:

$d_{21°}$ 0.9343 and $d_{23°}$ 0.9303; α_D — 34.8°; $n_{D21°}$ 1.4873 and $n_{D24°}$ 1.4800; acid v. 0.28 and 1.5 per cent.; ester v. 7.3 and 15.9 per cent.; alcohol content 12.9 and 21.4 per cent.

A1. Leaves, budding stage:

$d_{21°}$ 0.9776 and $d_{23°}$ 0.9271; α_D — 24.6 and 44.8°; $n_{D21°}$ 1.4923 and $n_{D23°}$ 1.4899; acid v. 2.36 and 0.1 per cent.; ester v. 14.0 and 14.3 per cent.; alcohol content 14.0 and 14.9 per cent.

B1. Leaves, flowering stage:

$d_{21°}$ 0.9383 and $d_{24°}$ 0.9224; α_D — 31.8 and 38.4°; $n_{D21°}$ 1.4887 and $n_{D24°}$ 1.4830; acid v. 0.25 and 1.7 per cent.; ester v. 7.7 and 17.1 per cent.; alcohol content 10.0 and 9.7 per cent.

C1. Leaves, fruiting stage:

$d_{21°}$ 0.9634; α_D — 12.6°; $n_{D21°}$ 1.4902 and $n_{D23°}$ 1.4868; acid v. 1.70 and 0.36 per cent.; ester v. 11.9 and 18.2 per cent.; alcohol content 6.1 and 28.0 per cent.

A2. Tops, budding stage:

$d_{21°}$ 0.9351 and $d_{23°}$ 0.9260; α_D — 30.4°; $n_{D21°}$ 1.4906 and $n_{D23°}$ 1.4908; acid v. 0.14 and 0.20 per cent.; ester v. 5.9 and 12.4 per cent.; alcohol content 9.9 and 17 per cent.

B2. Tops, flowering stage:

$d_{21°}$ 0.9429 and $d_{24°}$ 0.9219; α_D — 27.6 and 39.6°; $n_{D21°}$ 1.4898 and $n_{D24°}$ 1.4835; acid v. 0.64 and 1.30 per cent.; ester v. 10.3 and 18.8 per cent.; alcohol content 12.9 and 17.9 per cent.

C2. Tops, fruiting stage:

$d_{21°}$ 0.9421; α_D — 20.4°; acid v. 0.62 and 0.48 per cent.; ester v. 8.75 and 30.8 per cent.; alcohol content 7.7 and 50.2 per cent.

After heavy frosts, experiments in order to determine the effect of freezing were made with herb gathered on November 18th and which, being a second growth, had not yet reached the budding stage. The material consisted in the main of leaves and stems. The oil from the frozen plants distinguished itself by low specific gravity, low refraction and, above all, low rotation.

Yield, physical and chemical properties of spearmint oil from frozen and unfrozen plants.

	Frozen plants	Unfrozen plants
Yield (per cent)	0.11	0.13
Colour	deep golden yellow	yellowish green
Odour	mild characteristic, very pleasant	characteristic, very minty
Taste	bitter, slightly pungent, aromatic	bitter, very pungent, aromatic
Specific gravity	0.9180 at 24°	0.9252 at 23°
Rotation in 50 mm. tube (degrees)	— 4.7	— 27.5
Refraction	1.4771 at 25°	1.4822 at 23°
Solubilty in 80 per cent. alcohol (volume)	0.5, clear in excess	0.6 turbid in 2 or more volumes
Acid v. calcd. as acetic acid (per cent.)	0.79	0.85
Ester v. calcd. as acetate of $C_{10}H_{18}O$ (per cent.)	25.90	8.75
Alcohols calcd. as $C_{10}H_{18}O$ (per cent.)	19.26	12.22

Staranise Oil. The American Consul General in Hong Kong[1]) reports that the exports of staranise seed and oil decreased in a remarkable manner, in 1918. The declared exports of staranise oil to the United States in 1917 came up to 277787 lbs. to the value of 254833 Dollars, as compared with only 52328 lbs. to the value of 45355 Dollars in 1918. Scarcely anything was shipped to Europe. The prices remained fairly low during the first months of 1918 and there were some transactions, but when there was a rise later on, the American and other buyers refused to agree to it. The quotations were steady between 0.74 and 1.08 Dollars per lb.

It occasionally happens that staranise oil is adulterated with fatty oil[2]). M. S. Salamon and C. T. Bennett[3]) have recently stated that a consignment of staranise oil contained about 10 per cent. of a fatty oil. Two samples of the suspected article were investigated

[1]) *Handelsberichten (Den Haag)* **13** (1919), 362. — [2]) *Report* October **1912**, 105. — [3]) Perfum. Record **9** (1918), 324.

more thoroughly, one (I) being steam-distilled, the other (II) being distilled under reduced pressure and thus freed from the fatty oil. The properties of the oils were as follows:—

	I		II	
	originally	purified	originally	purified
$d_{20°}$	0.9814	0.9842	0.9804	0.9838
α_D	0	+ 0.3°	schwach +	schwach +
$n_{D25°}$	1.5495	1.5567	1.5470	1.5555
Solidification point	1.57°	17.2°	15.0°	16.8°
Melting „	17.6°	19.2°	17.1°	18.7°

The original oils were not easily soluble, whereas the purified ones showed normal solubility in alcohol 90 per cent. As it had been suggested from another side that the fatty oil might be the natural fixed oil contained in the anise fruits mechanically carried over in the distillation of the oil, the authors extracted some fruits with petroleum ether, volatilized the essential oil and then determined the constants (III and IV) of the fatty oils. They were evidently not identical with the fatty oils separated from the abnormal samples of staranise oil (I and II):—

	I	II	III	IV
$d_{20°}$	0.9492	0.952	0.940	0.923
$n_{D25°}$	1.4717	1.4745	1.4790	1.4700
Acid v.	0.4	3.0	—	—
Saponification v.	215.6	208.4	180.7	192.6
Iodine v.	37.9	35.5	105.3	97.4
Melting point	20 to 23.5°	22.23°	—	—
	Isolated fatty acid			
Melting point	22.8°	23°	41 to 42°	36°
Iodine v.	37.6	29.9	114.2	—

According to the authors, there still remains the possibility that the fatty oil might be derived from the leaves of the staranise, but the figures mentioned indicate clearly that the abnormal oils had been adulterated with a vegetable tallow.

Tea Oil. Aromatizing German tea is a difficulty, which, however, has been solved completely, according to O. Braemer[1]). All attempts to produce the aroma in German leaves through fermentation, in a similar way as with Chinese tea, failed, although an improvement of the taste was obtained. An only fermented product has only lost the so-called herbaceous taste, but never gets the slightly bitter and astringent typical taste of black tea and its aroma, still less its stimulating action. However, an appropriate and properly prepared leaf can be imbued with the full aroma of black tea by adding to it some artificial tea oil. As stated by the author elsewhere[2]), a product is thus obtained which does not distinguish itself in taste, aroma or appearance from the infusion from genuine Chinese tea. The tea oil is produced with the aid of bacteria[3]), the difficulty being that it is solely possible by exact control of the nutritive solutions to obtain and keep the bacillicultures pure, as the occurrence of so-called "false yeast" may spoil the whole result. The tea bacillus shows a very great tendency to degenerate.

[1]) *Heil- und Gewürzpflanzen* **2** (1919) 249. — [2]) *Ibidem* **2** (1918) No. 8. — [3]) Comp. Wangel, *Chem.-Ztg.* **27** (1903), No. 23.

Turpentine Oil. In a paper on the chemical industry and the raw marerials of Greece E. Sakellarios[1]) deals, *inter alia*, with the production of spirits of turpentine and of rosin and points out how important this industry is, the significance of which must not be under-rated. The total annual production of turpentine spirits in Greece amounts to 3 million kilograms; according to the method of production and the origin of the gum it contains 80 to 95 per cent. pure *d*-pinene (α_D up to $+48°$). The total amount of rosin produced annually reaches 12 to 13 million kilograms.

In 1916 a firm has been established at Athens commanding a capital of 2 million drachms and occupying itself with the production of turpentine spirits, rosin, essential oils, and ethers. During the blockade by the Allied Powers, pure turpentine oil (100 per cent.) was used for illuminating purposes, and when mixed with 2 per cent. ether as substitute for benzene.

The Forest Authorities in the Punjab[2]) report on the production of rosin and turpentine in this district. During the year closing with June 30, 1918 the Jallo works, founded in 1914, produced 16426 maunds rosin and 46709 maunds turpentine[3]). The Governor has consented to reduce the selling-price of rosin and turpentine of Jallo origin by one-sixth compared with the price fixed for foreign brands. The turpentine industry is believed to expect a brilliant future. In course of the year, an area of only 14521 acres was tapped, but it is expected that when the principal difficulties have been overcome, this area may be extended, in the Punjab as well as in the North-western Province, to the five-fold amount, thus raising the yield of rosin and turpentine in the same degree. The chief obstacles barring a rapid extension of this industry were lack of labour and the transportation difficulties between the woods and the railway stations.

Numerous methods have been worked out for the *determination of turpentine oil and the identification of its adulterations*, amongst them the process employing mercurous and mercuric acetates which we dealt with occasionally in our *Reports*[4]).

Balbiano[5]) studied the action of aqueous mercuric acetate on pinene and came to the result that the acetate forms no addition-product with pinene, but acts as oxidizing agent. This opinion is disapproved by J. Tausz[6]), who reports hereon in a paper giving several methods of estimating turpentine oil by means of double compounds with mercuric acetate. Tausz enumerates not less than eight different processes and describes in detail an acidimetric, a gravimetric, and a volumetric method. Another method worked out by Tausz in community with H. Wolf for the estimation of terpenes possibly present in crude petroleum has not been described further; by its aid it was easily possible to detect even 0.008 per cent. turpentine oil in mineral oils, but no terpenes were found thereby in crude petroleum[7]).

When testing turpentine oil according to the *acidimetric method* Tausz proceeds as follows: — The solutions required are methylalcoholic potash solution and methyl-alcoholic sulphuric acid, both about decinormal (they need not be standardized exactly); saturated methylalcoholic mercuric chloride solution, also saturated potassium bromide or sodium chloride solution. For standardizing the solutions 10 cc. pure turpentine oil are placed in a 100 cc. measuring flask and filled up with methyl alcohol; 10 cc. of

[1]) *Chem. Industrie* **41** (1918), 230. — [2]) *Nachr. f. Hand., Ind. u. Landw.* **1919**, No. 61, p. 3. Comp. *Report* October **1918**, 47. — [3]) Probably, it is the case of turpentine *oil*. — [4]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 29. — [5]) *Berichte* **48** (1915), 395; *Report* October **1915**, 77. — [6]) *Chem.-Ztg.* **42** (1918), 349. — [7]) Comp. p. 130 of this *Report*, where the formation of *cyclo*linaloolene as a degradation-product of a hydrocarbon from a fish oil is described. As is well known, fish corpses, according to Engler, are said to have played an important part in the formation of petroleum.

of this solution are mixed with 50 cc. saturated methylalcoholic sublimate solution and 50 cc. methylalcoholic potash, then 100 cc. water are added, with constant agitation, and the mixture is set aside in a cupboard protected from light. After exactly one hour a few drops of phenolphthalein solution are added and sufficient potassium bromide or sodium chloride solution until the liquid turns red. Then the sulphuric acid is added, with strong agitation, until the red coloration of the indicator disappears. The same test is carried out with 10 cc. of the turpentine oil under examination. In case more sulphuric acid is consumed, the sample is adulterated. For calculation purposes, a blank test, *i. e.*, without turpentine oil, is carried out. This test requires, say, 46.4 cc. sulphuric acid. With the pure turpentine oil, 4.2 cc. acid were needed, with the oil under examination 15.3 cc. The latter, therefore, contains less pinene than the pure oil, since less acid has been formed during the reaction. With the pure oil, the amount of the acid formed is $46.4 - 4.2 = 42.2$ cc., with the test sample $46.4 - 15.3 = 31.1$ cc. Turpentine oil of 100 per cent. yields 42.2 cc. acid, the sample of x per cent. yields 31.1 cc., $x = 73.7$. For sake of proof, the author mixed turpentine oil with a high-boiling benzine fraction of a Borneo petroleum occurring in trade also as substitute for turpentine. The results obtained thereby were in good accord, as appears from a table in the original paper.

The adulterant used in the experiments recorded hardly reacts with mercuric acetate at ordinary temperature. Pinolin (*Harzessenz*, light rosin oil) yields such low acid values that it can be at once distinguished from turpentine oil. Yet, in case the adulteration with pinolin exceeds 40 per cent., the method shows a higher amount of adulterant than is actually present; in such cases the flasks must be agitated very strongly, best on a shaking machine, in order to ensure greater accuracy. For exact determinations the standardization should be carried out not with 100 per cent. terpentine oil, but with an oil whose percentage is approximately equal to that of the adulterated sample. With turpentine oil containing limonene the titration must be performed after 24 hours' standing, but, as Tausz observed, this does not come into consideration with ordinary turpentine oil.

The process described by Tausz as the *volumetric method* has been worked out by W. Peter and is based on the well-known fact that pinene is oxidized on boiling with mercuric acetate. The oil under examination is boiled for three hours on the water-bath with aqueous mercuric acetate solution — later experiments showed that small amounts of methyl alcohol highly accelerate the reaction —, then the unattacked hydrocarbons are removed by steam and their weight is ascertained. It is impossible to recover the hydrocarbons used as adulterants quantitatively. For this reason the constant of the reaction is determined by boiling 10 or 15 cc. of cumene (previously purified by treatment with mercuric acetate) with mercuric acetate under a reflux condenser and finally distilling off the hydrocarbon with steam. If from 10 cc. cumene, 9.8 cc. are recovered, the constant of the reaction is 0.2 cc. The applicability of this method has been tested by Tausz with turpentine oils mixed with known amounts of hydrocarbons, when very good results were obtained.

Finally, a *gravimetric method* is described. The author examined the question whether the amount of the mercurous salt formed remains constant. It was proved that each hydrocarbon yielded a certain constant amount of mercurous salt, which, however, was not in stœchiometric proportion with the weight of the hydrocarbon employed. Hence, it is admissible to draw conclusions as to the amount of hydrocarbon present from the weight of mercurous salt only in such cases where the hydrocarbon is known. In this case the amount of mercurous salt is divided by a certain number which was ascertained for numerous hydrocarbons. The examination of turpentine

spirits shows all the preliminary conditions which have to be observed in this method. The *modus procedendi* is as follows: —

5 cc. pure turpentine spirits are dissolved to 100 cc. in methyl alcohol, the same is carried out with 5 cc. of the turpentine spirits under examination. Of each of these solutions, 5 cc. are transferred by means of a pipette into thick-walled bottles of about 200 cc. capacity, then 50 cc. saturated aqueous mercuric acetate solution are added to each, the bottles heated for 4 hours in boiling water, then cooled down and the mercurous salt separated out is filtered off; the latter is washed with wather, alcohol, and ether, dried and dissolved in dilute nitric acid (1 : 1). By addition of salt solution mercurous chloride is thrown down which is filtered off after several hours' standing, then washed, dried, and weighed. The calculation of the result is carried out in the following manner: — a is the pure turpentine oil, b the oil under examination. 1 cc. of a yields α g. of Hg_2Cl_2; 1 cc. of b. β g. Hg_2Cl_2. When $\alpha = \beta$, the oil analysed is pure; when $\alpha > \beta$, it is adulterated; *e. g.*, $\alpha = 9.35$ g., $\beta = 8.2$ g. Hg_2Cl_2. Oil of 100 per cent. yields 9.35, oil of x per cent. 8.2 g. $x = \frac{100 \times 8.2}{9.35} = 87.7$ per cent.

In cases of exact analyses it is recommended to weigh the oil in small glass pearls and to crush them in the boiling flask. When only small quantities are analysed the blank test is carried out and the Hg_2Cl_2 possibly thrown down must be subtracted. Of course, the determination of the mercurous salt formed may be carried out by any other method.

As to the applicability of the three methods, Tausz believes the acidimetric method to be very expedient whenever many determinations are to be carried out, also in cases when only small quantities of oil are available. The volumetric method is preferred in cases where the nature of the adulterant is to be ascertained; the gravimetric method enabled the author to examine even a very small quantity of oil.

Tausz finally remarks that these methods are equally of use in case of other terpenes.

Pharmacological Notes on turpentine oil. — Amongst the skin diseases which owing to the war have come into appearence more than ever, sycosis, or barber's itch, is one of the most dangerous. For treatment of superficial as well as of deep sycosis, M. X. Müller[1]) recommends injections of turpentine oil such as von Klingmüller uses with inflammations and suppurations: —

Rp. *Ol. terebinth.* 5.0
Paraffin. liqu. 20.0
M. D. S. For external use. For injections.

Are to 2.5 cc. of this solution to be injected hypodermically into the seat, after previously cleansing of the skin with benzine or carbon tetrachloride.

Other authors report equally favourably on the action of turpentine oil in skin diseases.

Von Klingmüller[2]) employs a 20 per cent. solution of rectified turpentine oil in olive oil and injects 1/4 to 1/2 cc. one to two cross-fingers below the upper outer margin of the pelvic bone right deep down to the bone. The injections may be repeated in intervals of a few days as often as desirable. The success was particularly striking in cases of gonorrhoic complications, furunculosis, folliculitis, impetiginous skin diseases, *acne vulgaris*, and abscesses of the perspiratory glands. Good results were sometimes

[1]) *Münch. med. Wochenschr.* **1918**, 697; *Vierteljahrsschr. f. prakt. Pharm.* **15** (1918), 90. — [2]) *Münch. med. Wochenschr.* **1918**, 896; *Therap. Monatsh.* **32** (1918), 467.

observed in cases of *pityriasis rosæ, lichen ruber, lupus erythematodes*, in diseases of the bladder and renal capsule. Recently it had been found that the influence was also favourable with tubercular glands of the throat and with scrophuloderma. One injection is generally sufficient to get rid of the itching in infantile scrophulus. How it acts has not yet been explained satisfactorily.

Equally good results have been observed by A. Grabisch[1]) by making use of von Klingmüller's technique.

F. M. Meyer[2]) tested von Klingmüller's treatment with 70 patients. He used a 20 per cent. solution of turpentine oil in groundnut oil for intragluteal injection, mostly in doses rising from 1/2 to 2 cc., and repeated the injection from 4 to 4 days, provided no rise of body temperature followed which was regarded as counterindication stopping further treatment. The reason why in one case fever set in, and not in other cases, could not be ascertained. In general, the injections were tolerated very well, in contradiction to von Klingmüller no reaction was noticed. In order to ensure complete recovery it was necessary to inject more frequently (up to 12 times) as von Klingmüller did, possibly because local treatment was abandoned. The treatment was effective with dermatosis with marked purulent discharge, especially with deep sycosis, furthermore with furunculosis and cases of ulcers of the lower leg. Besides, one serious case of chilblains of the palms was treated with marked success.

Finally, J. Sellei[3]) observed good results with superficial festering of the skin and impetiginous exanthema; not quite 50 in cases of pyodermia and furunculosis; pruritus was sometimes influenced favourably. With deep eczema the action was not quite so beneficial, even less so with chronic eczema. A drawback of the treatment is that it causes fevering and requires sometimes a great number of injections. The author made use of an oily solution (20 to 40 per cent.) of 0.1 to 0.2 g. turpentine oil for intragluteal injection.

Wood turpentine oil. — We beg to supplement our former communication on the occurrence of a new terpene in so-called Finnish turpentine oil observed by Aschan[4]) by stating that according to the same author[5]) this terpene, on treatment with amyl nitrite and hydrochloric acid, yielded pinene nitrosochloride.

When examining Finnish turpentine (oil?) Aschan[6]) tried to find out new methods for preparing terpine from pinene and dipentene. In a preliminary experiment he studied the action on turpentine oil of sulphuric acid of different strength, cooling being omitted. The explanation of the results was that mostly terpine is formed, at ordinary temperature, as intermediary product whenever pinene is transformed into dipentene by means of acids, but that owing to the high concentration and the possibility of internal rise of the temperature this formation of terpine is restrained in favour of a dehydrating action with formation of dipentene. Good stirring and cooling is essential thus protecting the terpine hydrate formed from being decomposed by the acid. When using sulphuric acid of 45 per cent. and with intense stirring, 53.2 per cent. of the theoretical amount of terpine could be isolated; the temperature must hereby be kept the whole time at + 1°. *Trans*-terpine may result as by-product. β-Pinene, when treated with 45 per cent. sulphuric acid, yields likewise terpine.

Aschan ascertained furthermore that terpine is formed by hydration of dipentene when treating one part of the terpene with 6 parts of sulphuric acid of 55 per cent.

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[1]) *Derm. Wochenschr.* **1918**, 624; *Therap. Monatsh.* **32** (1918), 468. — [2]) *Berl. Klin. Wochenschr.* **55** (1918), 880; *Therap. Monatsh.* **32** (1918), 468. — [3]) *Deutsche med. Wochenschr.* **44** (1918), 1028; *Therap. Monatsh.* **32** (1918), 468. — [4]) *Chem. Ztg.* **40** (1916), 235. — [5]) *Technikern*, Oct. 10., **1915**; *Chem. Zentralbl.* **1919**, I. 284. — [6]) *Bidrag till kännedom af Finlands natur och folk* **77** (1918), No. 1; *Chem. Zentralbl.* **1919**, I. 284.

at — 6°. The crude product obtained is particularly pure; as by-product, *trans*-terpine may occur also here.

Transformation of terpine hydrate into terpineol by splitting off water is effected best by action of 0.5 per cent. oxalic acid. The formation of terpineol from pinene by aid of formic acid passes off so favourably that the author expects this process to work on a commercial scale. A nearly quantitative yield of terpine hydrate from terpineol was effected by treatment with 5 parts of 40 per cent. sulphuric acid with stirring and ice-cooling.

Aschan's experiments proved that terpine hydrate may be prepared, in satisfactory yield, from the fraction b.p. 155 to 167° of Finnish turpentine oil, containing the pinene-like terpenes.

In addition, Aschan[1]) makes some statements as to the higher-boiling components of Finnish turpentine oil. In a sample of the oil as well as in a commercial distillate (both prepared from *Pinus sylvestris*) he found a *terpene alcohol* and cadinene, where, however, the question remains still to settle whether cadinene occurs as such in the fraction b.p. 125 to 130° (9 mm.), or whether it was formed from another sesquiterpene on addition of hydrogen chloride gas.

He obtained furthermore from Finnish turpentine (oil), obtained from the tar distilleries as well as from distilling the resinous products, fractions boiling from 210 to 220° and about 260° and consisting probably of a terpene alcohol and a sesquiterpene. The same fractions were found in a by-product resulting from the preparation of pine rosin. Aschan obtained an *unsaturated terpene alcohol* $C_{10}H_{17}OH$, which was not identical with ordinary terpineol and probably was a mixture of terpineol with other terpene alcohols. In addition, he isolated a *sesquiterpene* $C_{15}H_{24}$ (b. p. 260 to 263° [760 mm.]; $d_{40}^{20°}$ 0.9187) yielding cadinene hydrochloride (m.p. 117 to 118°) with hydrogen chloride, which proved to be unsaturated owing to its behaviour towards permanganate solution or bromine. Since it boiled 10° lower than cadinene, it was evidently not identical with that terpene.

Finally, Aschan mentions a sesquiterpene fraction from the volatile constituents of pine rosin; they contained a new body, the dihydrochloride $C_{15}H_{26}Cl_2$ of which melted at 85 to 86°. It is possibly the case of a bicyclic sesquiterpene related to cadinene.

American pine tar oil yields, on distilling with steam, according to E. J. Millard[2]), about 40 per cent. of a brown oil *(Ol. picis rectificatum)* (d 0.920) smelling of tar and showing weak acid reaction. On treatment with soda solution and by following rectification a light oil (d 0.881) has obtained which was nearly colourless and smelled only slightly of turpentine oil.

Amongst the endeavours of the present time notice must be taken of the attempts to obtain home-grown pine-resin in Germany, facts to which we referred repeatedly[3]). For the present it is impossible to say which of the various sources for resin recommended by the authors mentioned will prove to be profitable. In this connection we mention a publication of J. E. Brauer-Tuchorze[4]), where the preparation of oil and rosin from pine wood is described. Since, however, the work contains nothing new and furthermore it is not quite clear to which species of pines the work refers, we content ourselves with this note.

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[1]) *Ibidem* **77** (1918), No. 2; *Finska Kemistsampfundets Meddelanden* **1916**, **1918**; *Chem. Zentralbl.* **1919**, I. 284, 285. — [2]) *Pharmaceutical Journ.* **100** (1918), 28; *Chem. Zentralbl.* **1918**, II. 37. — [3]) Comp. *inter alia* our *Bericht* (German edition) **1918**, 50. — [4]) *Seife* **3** (1918), 182.

On p. 62 of our *Report* **1917** we described a method for quick-maturing of wood consisting in treating freshly-felled wood in a special apparatus, at certain temperature, with organic solvents, whereby the water is expelled and fats, oils, and resins are dissolved. Further particulars as to the necessary plant are to be found in a paper by E. R. Besemfelder[1]) who points out the economical importance of the process.

Sulphite turpentine oil. — As is generally known, the principal constituent of this oil (somewhat related to wood turpentine oil) is *p*-cymene. For this reason we refer to a series of publications dealing with the synthesis of several important preparations from that oil.

On p. 148 of our *Report* **1917** we discussed a paper by E. Boedtker and O. Halse[2]) on the action of aluminium chloride on mixtures of benzene and cymene. In this reaction there is also formed toluene. Since during the war great quantities of toluene were required, A. S. Wheeler[3]) repeated in part the work of the aforesaid authors. The spruce turpentine, a waste product of the sulphite process of making spruce wood paper pulp (from *Abies canadensis*, Michx.), served as surce of toluene. The spruce turpentine, an oil resembling somewhat wood turpentine oil, consists largely of *p*-cymene. Wheeler purified the oil by distillation with superheated steam, the vapour being bubbled through hot 10 per cent. caustic soda solution and then condensed in the usual way. The crude turpentine oil was pale red, after condensation water-white. When no caustic lye is used for purifying the oil the distillate is lemon-yellow in colour. The oil was separated from the water and shaken several times with 0.5 per cent. potassium permanganate solution and then twenty times with one-sixth of its volume of concentrated sulphuric acid. Then the oil was shaken with water, dried over calcium chloride, and distilled over sodium; b. p. 177 to 177.5°. With this cymene, Wheeler repeated the experiments of Boedtker and Halse, but did not obtain the good yields of toluene as these authors did; 90 g. cymene, 900 g. benzene and 4.5 g. aluminium chloride boiled for ten hours on a water-bath gave 15 cc. distillate of b. p. 109 to 113° (toluene) and 43 cc., b. p. 151 to 154° (cumene). In a second experiment 88.5 g. cymene, 885 g. benzene, and 4.5 g. aluminium chloride yielded, after ten hours' heating on the water-bath, 22 cc. oil, b. p. 108 to 112° and 52 cc. of b. p. 149 to 154°. From the toluene fraction of the first experiment Wheeler prepared T. N. T. of the m. p. 80 to 80.5°.

In Wheeler's opinion, cumene must not be regarded as a waste product, since it may be oxidized to benzoic acid.

Besides for the preparation of toluene, oils containing reasonable amounts of cymene, such as the so-called sulphite turpentine oil, may be used for the manufacture of carvacrol[4]). On this subject A. W. Schorger[5]) gives a report. He believes that annually about 750000 gals. of sulphite turpentine oil are available in the United States and Canada as by-product of the manufacture of pulp. The wood employed mostly is that of the spruce, then of the balsam and hemlock fir.

For the purpose of identifying cymene Schorger recommends as the simpliest method the preparation of cymene sulphamide (*viâ* the sulphonic acid) melting according to his statements at 114°, the m.p. given in the literature being 115 to 116°. Although this method, in itself, is nothing new[6]), we give an abstract of the process adopted by

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[1]) *Chem. Ztg.* **43** (1919), 4. — [2]) *Bull. Soc. chim.* IV. **19** (1916), 444. Comp. also A. W. Schorger, *Journ. Amer. chem. Soc.* **39** (1917), 2671; *Report* October **1918**, 117. — [3]) *Journ. ind. eng. Chemistry* **10** (1918), 359. — [4]) As to the preparation of cymene from sulphite liquor and sulphite turpentine oil, *vide Report* April **1915**, 83; October **1917**, 74, 148. — [5]) *Journ. ind. eng. Chemistry* **10** (1918), 258. — [6]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I. p. 284.

Schorger. 50 g. Cymene and 100 g. fuming sulphuric acid (with 10 per cent. SO_3) are shaken until solution is effected, and after cooling the mixture is poured into a separating funnel, and about one-third of its volume of cold water added. Two layers are formed, the upper one consisting of cymene sulphonic acid. This acid is dissolved in about 5 liters boiling water, the solution neutralized with barium carbonate, and the barium sulphate filtered off. After removal of the Ba-salt of cymene-2-sulphonic acid separated off, the filtrate contains the salts of cymene-3-sulphonic and of a disulphonic acid which may be separated by alcohol. From 50 g. cymene, 79.9 g. 2-sulphonate, 14.6 g. 3-sulphonate, and 4.2 g. disulphonate were obtained. 35.4 g. of the dry 2-sulphonate were heated with the equal amount of phosphorus pentachloride and from the chloride the amide was formed by heating with ammonia in the ordinary way.

Schorger regards the method of identifying cymene by oxidation to *p*-hydroxy-*iso*propyl benzoic acid as somewhat tedious. Equally good results are obtained when only half the amount of potassium permanganate given by Wallach[1]) is used[2]). A superior means for the identification of *p*-cymene is the ready reaction with chlorosulphonic acid. The hydrocarbon is gradually mixed with the equal volume of chlorosulphonic acid, with constant shaking, the mixture is then treated in a separating funnel with water, extracted with ether, and the ether extract washed with water to remove inorganic acids. After evaporation of the solvent the cymene chlorosulphonic acid is transformed to the sulphamide by heating with concentrated ammonia on the water-bath. The sulphamide is recrystallized from hot water. The method is rapid and the yields are excellent.

For the preparation of the sulphamide of *p*-hydroxy*iso*propyl benzoic acid Schorger heats 10 g. cymene sulphonamide with a solution of 30 g. potassium permanganate in 2 liters of water; the manganese sludge is filtered off, the filtrate evaporated to dryness and extracted with hot 95 per cent. alcohol. The latter is evaporated and the residue extracted with hot absolute alcohol. On cooling, the potassium salt of *p*-hydroxy*iso*-propyl benzoic acid sulphamide was deposited as warty mass.

In order to obtain carvacrol from *p*-cymene, the calcium, barium, or sodium salt of cymene sulphonic acid were fused in a nickel dish with alkali (KOH, K_2CO_3, or NaOH) dissolved in a minimum amount of water at temperatures varying between 290 and 350°. The yields were poor, but Schorger believes that satisfactory yields can be obtained from larger apparatus capable of control. The carvacrol thus prepared was identified by means of nitrosocarvacrol, m.p. 153 to 154°. It was found that the nitrite was insoluble in petroleum ether, and this property afforded an easy means of purification: the nitroso-compound was dissolved in a minimum amount of chloroform which was slowly dropped, with stirring, into a considerable volume of petroleum ether. The precipitate was finally crystallized from alcohol.

In connection with the preceding we wish to inform our readers on a lengthy publication by A. W. Hixson and R. H. Mc. Kee[3]) *on the conditions essential for the commercial manufacture of carvacrol.*

The authors point out that thymol, closely related to carvacrol, is the principal ingredient in many antiseptic preparations and is used as a specific for hookworm

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[1]) *Liebig's Annalen* **264** (1891), 10. — [2]) We point out that also several terpenes are transformed into *p*-cymene by the action of sulphuric acid, so that the occurrence of *p*-cymene after treatment with fuming sulphuric acid cannot be regarded as a proof for its presence in the original oil. For this reason Wallach made use of the oxidation to *p*-hydroxy*iso*propyl benzoic acid. — [3]) *Journ. ind. eng. Chemistry* **10** (1918), 982.

disease[1]) in large quantities, the demand thus having become so great that the supply from the present sources is entirely inadequate[2]). Attempts to prepare synthetical thymol on a commercial scale have hitherto failed. The numerous syntheses of carvacrol, which for medicinal purposes might be used instead of thymol, are, in the opinion of the authors, impracticable with exception of the patented process of Mc. Kee[3]) based upon the use of the above-mentioned spruce turpentine oil.

On the whole, the authors' process of preparing carvacrol resembles Schorger's above-described method. The principal features of their process are as follows: —

1. Formation of cymene-*1*-sulphonic acid by treating spruce turpentine oil with sulphuric acid;
2. Removal of the excess sulphuric acid used in 1. and formation of calcium cymene sulphonate by treatment with finely divided limestone;
3. Formation of sodium cymene sulphonate in solution and removal of calcium as carbonate by treating with soda ash;
4. Formation of sodium carvacrolate by fusing the sodium cymene sulphonate with caustic soda;
5. Formation of carvacrol by treating the fusion products of 4. with sulphuric acid.

All the materials used in the experimental work were of standard commercial purity, such as can always be obtained on the market, with the exception of spruce turpentine oil, which up to the time has had no commercial value. The oil used gave on distillation the following fractions: below 171.5°, 3.33 per cent. by volume; 171.5 to 178.5°, 83.34 per cent.; above 178.5°, 13.33 per cent.

When sulphonating, the prime variables are: 1. the strength of the acid; 2. temperature; 3. time; 4. proportional amount of acid; 5. amount of stirring, and 6. type of sulphonating vessel.

The adoption of 66° Bé. sulphuric acid as used for the sulphonation of benzene in phenol manufacture gave the best results. The most favourable temperature, as was proved in numerous experiments, was between 90 and 100°. As to the time required, 4 hours were sufficient, provided that intense stirring took place and a temperature of 96° was maintained. The best method is to sulphonate the spruce turpentine with the equal amount of acid; with less acid complete sulphonation could be obtained, but the time required was greatly increased. Good stirring is essential for obtaining good results. In a cast-iron vessel, with a stirrer running 500 to 600 runs pro minute the sulphonation of 300 cc. spruce turpentine with 300 cc. sulphuric acid was complete in from $3^1/_2$ to 4 hours, at 96 to 98°; the iron of the vessel was hardly attacked. When sulphonation was complete the mixture separated, on standing, into two layers. The lower, lighter coloured layer contained the greater portion of the excess sulphuric acid and about 20 per cent. of the total amount of the cymene sulphonic acid. The upper darker coloured layer contained the greater part of the cymene sulphonic acid, some sulphuric acid, and impurities resulting from the action of the acid on the impurities in the spruce turpentine. When the materials were hot the formation of the layers took place rapidly. In the cold, or on prolonged standing at room temperature the cymene sulphonic acid was separated off from the upper layer as a crystalline substance. It showed the m.p. 50 to 51°, as stated in the literature. Furthermore, the upper layer contained small amounts of sulphur. By way of experiment the amount of water was

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[1]) Comp. *Report* April **1915**, 50; **1916**, 61. The latest investigations seem to prove the superiority to thymol of American wormseed oil in fighting hookworm disease. Comp. also pp. 61 and 113 of this *Report*. — [2]) Probably owing to the war. — [3]) U. S. P. No. 1265800.

ascertained as was necessary to obtain a maximum of cymene sulphonic acid in the upper layer. The quantity of water required was one-fifth of the total volume of the mixture. Generally, it will not pay to recover the free sulphuric acid from the lower layer.

The neutralization of the sulphonation products is effected by means of finely divided limestone or lime. In the former case, the evolution of carbon dioxide causes foaming. The calcium sulphate is removed by a filter-press, the filter-cake being worthless. Simultaneous neutralization of the sulphonation products and formation of sodium cymene sulphonate from the calcium salt may be effected by addition of sodium carbonate solution, the calcium sulphate and carbonate can then be removed by a single filtration. With these processes a minimum of water must be employed, for the reason of saving time in evaporating the solution of sodium cymene sulphonate. This solution is difficult to evaporate to dryness at atmospheric pressure, which may be perfected by applying a vacuum or a film dryer.

When fusing the sodium cymene sulphonate the problem was to determine *a*) the best fusion reagent, *b*) the proper fusion temperature, *c*) the most suitable type of fusion kettle, *d*) the time required for completion of the reactions, and *e*) the minimum amount of fusion reagent for obtaining the maximum yield.

The fusion apparatus used by Hixson and Mc. Kee was a cylindrical steel vessel $4^1/_2$ in. in diameter and 5 in. deep, the thickness being $^3/_{16}$ in. The cover was a steel plate with openings for the stirrer shaft and the thermometer. Heating was effected by placing the vessel in a bath containing a eutectic mixture of sodium and potassium nitrates, since by heating with a Fletcher burner it was not possible to control the temperatures closely enough. Commercial caustic soda was used with satisfactory success as fusing reagent. The best yields were obtained with fusion temperatures of from 360 to 370°. It is necessary to operate with the vessel covered, as otherwise carvacrol escapes and the fusion mass oxidizes and thickens. The experiments were started with 150 g. dry sodium cymene sulphonate and 450 g. caustic soda; the latter was fused first and the sodium cymene sulphonate added slowly. Addition of water enables to keep the fusion temperature lower, but offers no advantages. Fusions carried out at 360° yielded 48.33, 49.91, and 49.14 g. carvacrol, *i.e.*, 50.14, 52.31, and 51.60 per cent. At 370°, the yield was 50.65 per cent. Beyond 370°, the yield decreases. About 18 to 20 per cent. of the sodium cymene sulphonate are transformed into cymene, which when working on factory scale might be profitable to recover. During the fusion process two reactions take place: — *a*) formation of sodium carvacrolate and sodium sulphite, *b*) of cymene and sodium sulphate. In addition, other reactions pass off, as is evident from the formation of hydrogen, methane, and tarry products.

The best yield was obtained with fusion periods of from 4 to 6 hours. In these experiments a large excess of soda was used. Nevertheless, much less soda, even only the theoretical quantity, yielded equally favourable results.

It is also possible to fuse calcium cymene sulphonate with caustic alkali, thus saving one filtration and the sodium carbonate for the making of the sodium salt, but this would result in requiring more caustic necessary for the fusion, and in difficulties arising from the insolubility of the calcium sulphite formed. In this process, also cymene is formed.

Neutralization was effected by dissolving the fusions in 2 liters of water and adding an excess of dilute sulphuric acid (40° Bé) until sulphur dioxide was evolved. The acid must be added to the solution by leading it through a tube to the bottom of the vessel, as otherwise an excess of the acid on the surface reacted with the sodium sulphite in

that part before neutralization throughout was complete. In this case the evolution of sulphur dioxide was no proof for complete neutralization.

From the neutralized liquid the carvacrol may be extracted by shaking with benzene or preferably by steam-distillation, the distillation-water must also be shaken with benzene.

The carvacrol obtained by this process could be purified sufficiently and without difficulty by fractionation.

Guided by these laboratory-scale results the authors undertook to convert a larger amount (53 lbs.) of spruce turpentine into carvacrol and succeeded fairly well, the yield being 57.2 per cent. The fusion process, the most difficult operation to handle, gave only 13.7 per cent. of cymene. It was noted that dry sodium cymene sulphonate cannot be kept at open air, as it takes up moisture rapidly.

The time required for each operation was such that it could be completed within eight hours.

We cite here a paper published in an American periodical[1]) on the utilization for preparing toluene from the sulphite turpentine, a waste product of the sulphite pulp process. The Technical Association of the Paper and Pulp Industry studied this question and recommends a process worked out by the Hammermill Paper Co. The apparatus employed for the separation of cymene is described in short and an illustration thereof given; its new feature is in the main the addition of a second separator. The process is intended to raise the production of toluene, an object, however, which at present, the war being over, is probably of minor importance.

Equally, in Sweden the by-products occuring in the chemical treatment of wood-pulp play a great part in the economics of the factories, as appears from the following figures concerning the years 1913 to 1915[2]):—

	1913		1914		1915	
	kg.	Kroner	kg.	Kroner	kg.	Kroner
Cymene (sulphite pulp)	—	—	—	—	5954	1054
Turpentine, crude (sulphate pulp)	—	—	—	—	129528	27779
do., distilled (sulphate pulp)	311366	90413	347397	119050	386389	324042

Naturally, the war years of late gave a strong impetus for securing better yields of the by-products, since Sweden was cut off from foreign countries and could import neither rosin nor benzine, the industry thus being forced to resort to home products, when the sulphite spirits were the only substitute for benzine. The production of turpentine was raised, in 1916, up to 875000 kg.

Finally, we report on a paper by Th. Oertenblad[3]), who was unable to recover cymene from the waste sulphite liquor or from the condensed product after driving off the gases, but was successful in obtaining it from the "gassed" sulphite acid which resulted when the waste gases were introduced into weak fresh boiling liquors. From each ton of pulp 0.35 kg. cymene resulted; from fresh wood yield was by far higher.

The crude cymene was a yellowish brown liquid with greenish fluorescence, the colour being the darker the longer the hydrocarbon circulated in the process; d 0.88. It contained 80 to 85 per cent. pure *p*-cymene and 15 to 20 per cent. resinous substances, in addition to small amounts of ill-smelling organic sulphur compounds and fatty acids. Purification is effected by neutralization with quicklime and subsequent steam distillation, if necessary, also by fractional distillation.

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[1]) *Chem. Metallurg. Engineering* **18** (1918), 338; *Chem. Zentralbl.* **1919**, II. 61. — [2]) E. Moritz, *Wirtschaftsdienst* **4** (1919), 56. — [3]) *Teknisk Tidskrift* **1918**, No. 8; *Papierfabr.* **16** (1918), 717. According to *Chem. Zentralbl.* **1919**, II. 262.

Wormseed Oil, American. After the greatest exertions, we have succeeded in getting a small lot of a reliable oil from the United States, but it was in no way sufficient to satisfy the demand. The numerous users of this important vermifuge will have to arm themselves with patience for some time to come, for the quantities under way are also rather limited. This year's distillation is in full swing, but although nothing is known as yet about the result to be expected, it may safely be predicted that, owing to the active demand and the unfavourable rates of exchange, higher prices are to be reckoned with rather than lower ones.

The trade with American wormseed oil still presents the old aspect, *i.e.* all the samples submitted to us for examination in the course of last year were substitutes without exception, chiefly composed of eucalyptole, anethole, menthol and amyl acetate and in which the characteristic components of the genuine wormseed oil were conspicuous by their absence. When reading in the pharmaceutical press the numerous offers of vermifuges, prepared with American wormseed oil, one is bound to wonder whether the manufacturers have not in many cases been the victims of a shameless fraud. The good renown of the genuine oil is thus greatly injured.

We have often had an opportunity to give our opinion as to the value of wormseed oil as a vermifuge, but we want nevertheless to acquaint our readers with an article by J. C. Umney [1]), called Thymol *versus* Chenopodium Oil, although it results already from a communication of Schüffner and Vervoort [2]), published some time ago, on experiments made in Deli (Sumatra) with 1457 people, that chenopodium oil proved superior to all the other remedies.

Umney discusses the reports that have been published on the treatment of miners' hookworm disease in Fiji, Trinidad and the Seychelles.

The Trinidad Committee chiefly used thymol mixed with an equal quantity of sodium bicarbonate, both finely powdered. It was given in two equal doses at 6 a. m. and 8 a. m., being preceded the night before, and followed at 10 a. m., by a purge. The normal dose for an adult was 40 g. with a maximum of 60 g. Owing to children resenting the treatment, a preliminary aperient was abolished and at 6 a. m. one minim of oil of chenopodium for each year of apparent age was given and at the same time ½ oz. of castor oil. The number of cases treated with chenopodium oil was very small against those with thymol. Anyway the report states that the oil of chenopodium proved only half as efficient as thymol in rendering the patient's stool free from ova of hook-worms, but the chenopodium oil had the distinct advantage of removing *Ascaris lumbricoides* from a large number of the children.

Umney sees the very low efficiency of the chenopodium oil in the unusually small dose administered.

However, a very different account came from Fiji. During 1917, oil of chenopodium was exclusively used in the treatment of 1818 cases. There was no doubt, the report says, of the superiority of chenopodium oil compared with thymol or any other drug hitherto tried. It possesses the additional value that it is the most potent destroyer of the round worm and was used with the greatest success in the treatment of horses. The Tamanua hospital found the most efficient method for treatment in doses of usually 15 minims in capsule at 5.30, 6.30 and 7.30 a. m., preceded and followed by an aperient with no food whatever during the period of treatment. This is called

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[1]) *Perfum. Record* **10** (1919), 139. — [2]) *Münch. med. Wochenschr.* **60** (1913), 129; *Report* October **1913**, 108. See also *Reports* October **1916**, 61; April/October **1917**, 80; April/October **1918**, 52.

"intensive" method and one may be sure of obtaining a cure in 90 per cent. of patients after one treatment only. If the patients are kept very quiet lying down, there are no ill-effects. This method is most suitable for hospital use. Where patients cannot be kept under control and observation, the second capsule is omitted, but it is necessary to repeat the treatment several times. According to the report, chenopodium oil excels thymol in many respects, being less toxic, more efficient, not so costly, and of greater effect upon the ascarides, which are so often associated with the hook-worms. The failure of some men to obtain good results is attributed to the small dose employed and the method of administration. A regular scale of doses has been drawn up for the first two treatments, *viz.*, over 60 years of age, 20 minims, 21—60 years, 30 m., 11—20 years, 20 m., under 10 years, three drops for each year of age, pregnant women, 18 drops. The dose is slightly increased for those not cured by two treatments. After two treatments about 70 per cent. or more were cured. This percentage could be increased if the patients were more careful of their diet during the day of treatment; in patients obedient to advice, the cures after two treatments reached 85 per cent. Of the 1000 cures obtained in the first three months, 801 occurred after two treatments. 184 after four, and remaining 15 after five treatments.

Of 3088 infected persons found in Navua, 3010 were treated, of which 2794, or 92.8 per cent. were cured. If it was possible to carry out the treatment properly, there is no doubt that all could be cured.

In 1917, a campaign against ankylostomiasis was started in the Seychelles, when it resulted that about 90 per cent. of the population were infected. By the end of the year treatment had been given to practically two-thirds of the population of the island of Mahé, the improvement owing to the treatment being clearly visible in the general state of health.

As to further results in treating the hook-worm disease with wormseed oil, see p. 113 of this *Report*.

E. Oppikofer [1]) and P. Ryhiner [2]) report on cases of poisoning with American wormseed oil. According to them, 15 such cases are known so far, 10 of which ended with the death of the patient. In severe cases, the hearing remains considerably handicapped, whereas the other nerves of the brain do not seem to suffer. The doses for adults ought not to exceed 3 times 16 drops daily, those for children 3 times 8 drops daily on two consecutive days. Ryhiner has seen cases of poisoning even with these doses, for which reason he proposes to give to children, with intervals of one hour, as many drops as the child counts years of age. Two hours after the last administration an aperient should be given in liberal quantity.

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[1]) *Korrespondenzbl. f. Schweiz. Ärzte* **49** (1919), 161; *Therap. Monatsh.* **33** (1919), 279. — [2]) *Korrespondenzbl. f. Schweiz. Ärzte* **49** (1919), 360; *Therap. Monatsh.* **33** (1919), 279.

Chemical Preparations and Drugs.

Almond Oil, sweet. We have mentioned repeatedly that, owing to the present scarcity of sweet almond oil and other oils or fats, the manufacture of fatty oil from plum stones has been suggested, in which connection we discussed treatises of K. Alpers[1]) and F. Darvas[2]). In an article published by G. Kassner[3]) later on, the use of the kernels of the common plum *(Prunus domestica.* L., *Rosaceæ)* is also described. The oil obtained through pressing, from sound, ripe kernels was golden yellow, $n_{D20°}$ 1.4705, iodine v. 104.9. On cooling in a freezing mixture, only at $-15°$ some crystalline flakes separated, otherwise it only became a little thicker. The residues from the pressing were treated in the same way as the German Pharmacopœia prescribes for the preparation of bitter almond water, when an *"Aqua pruni"* was obtained, which answered the requirements of the German Pharmacopœia for *"Aqua amygdalarum amararum"*. The content of free hydrocyanic acid (not bound to the benzaldehyde) was below the maximum indicated as admissible.

Anethole. The use of phthalic ester as an adulterant has been altogether appalling in the year reviewed in this *Report*. A special activity in this domain has been displayed by a little Leipzig firm, which apparently adds this ester indiscriminately to all the oils, as we may safely conclude from a good many samples of all sorts of oils, which were adulterated in said way and, without exception, came from the firm in question. One of the products thus faked was anethole, which showed the following constants: $d_{25°}$ 1.0200, α_D — 0° 17′, solidification point + 8°, soluble in any quantity of alcohol 90 per cent. and in 5.5 vols. alcohol 80 per cent. The optical activity indicated that the product was no anethole, but aniseed oil. The excessive specific gravity, the low solidification point and the ready solubility led to the conclusion that the oil had undergone changes, such as may occur with either anethole and aniseed oil, when improperly stored. It was remarkable, however, that the oil was nevertheless colourless and had no smell of anisaldehyde, which is characteristic for altered aniseed oils, as referred to. This apparent contradiction was quickly explained on saponifying the product. Whereas aniseed oil does not contain any saponifyable constituents, the sample under investigation showed an ester value of 169.8. This proved the presence of an ester, which we characterized by isolating the acid parts of the oil. We thus obtained a solid acid, melting at about 197° and yielding on sublimation an anhydride melting at 130°. It was evident therefore that we had to deal with phthalic acid. According to the ester value mentioned before, the content of phthalate amounted to 29.4 per cent., calculated as dimethyl phthalate. It seemed to us that, in addition, traces of another ester were present.

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[1]) *Chem. Ztg.* **40** (1916), 645; *Report* October **1916**, 67. — [2]) *Zeitschr. d. allg. Österr. Apoth. Ver.* **54** (1916), 419; *Report* October **1917**, 87. — [3]) *Arch. der Pharm.* **256** (1918), 106.

Asafœtida. Like most drugs, asafœtida is sometimes adulterated. E. Claassen[1]) examined samples, in which there were white, brilliant particles to be recognized. On treating it with hot water and afterwards with a little alcohol, he obtained a residue, consisting of whitish, brilliant particles and of greyish ones with black spots. The former were calcite, the latter granite with black spots of amphibole. The sample contained 54.45 per cent. asafœtida, 35.51 per cent. calcite and 10.04 per cent. granite.

The adulteration of another sample amounted likewise to about 50 per cent. and consisted only of calcite.

Benzaldehyde. Owing to the absolute lack of genuine bitter almond oil, there is a very keen demand for benzaldehyde free from chlorine and it is a great calamity that it is difficult to obtain a product coming at least somewhat near to this requirement. The products offered of late as free from chlorine stood in no way the test, on the contrary, there were repeatedly samples which, judged by the former standard, had to be termed as raw, strongly chlorinated products. The absolute want of an article free from chlorine gradually led to the introduction of benzaldehydes "poor in chlorine" and to distinguishing even between "poor in chlorine" and "containing traces of chlorine". The question now was, up to what percentage a benzaldehyde might be considered as "poor in chlorine", on which subject the views vary considerably. An acceptable proposition was to fix certain limits and to introduce three qualities; *viz.*, free from chlorine, up to 0.02 per cent. chlorine and up to 0.2 per cent. chlorine, or simply to guaranty a certain content of chlorine.

This would be a solution, but it would then be necessary to know a method of determining the content of chlorine. This is the most important point, for the determination must be very exact and easily and quickly carried out. This applies quite specially to the wholesale trade, where it is often a question of deciding quickly which benzaldehyde out of a whole range of samples is to be purchased. Furthermore it is of the utmost importance that not only the chlorine in the nucleus but also that in the side chain be determined, as both positions are possible. Such a general method is still lacking, for with the small proportions of chlorine coming into consideration, a comparatively great quantity of benzalaldehyde must be tested, in which case the usual methods, as for instance that of Carius, are either not applicable at all, or they are far too complicated. In consequence, it is impossible to determine quantitatively the chlorine in the nucleus, so that one must be contented so far with the determination of that in the side chain, for which methods are known. It is true that this is of questionable value, as it may lead to consider as free from chlorine a strongly chlorinated product, if the chlorine is in the nucleus, or to establish a lesser percentage than is really present, if the chlorine is partly in the nucleus and partly in the side chain. We have tested of late a similar benzaldehyde, said to be free from chlorine, but containing rather a lot of chlorine in the nucleus and which therefore escaped the usual quantitative analysis.

It is evident that such a method does not help much, on the contrary, it is really quite unfit for our purpose, and if we here discuss it a little further it is only because benzaldehydes are now and then judged in commerce by this method. When boiling the benzaldehyde with alcoholic potash, the chlorine of the side chain combines with it to form potassium chloride, which can then be determined quantitatively. We proceed in the following way: 20 g. of benzaldehyde are boiled for about 8 hours, under a

[1]) *Americ. Journ. Pharm.* **91** (1919), 164.

reflux condenser, with 1 g. potassium hydroxide free from chlorine, dissolved in 20 cc. of alcohol. The mixture is then well shaken with 40 cc. of water, separated in a separating funnel and the remaining benzaldehyde shaken again with 40 cc. of water. About 100 cc. of liquid are thus obtained, which are acidulated with 2 cc. of concentrated nitric acid. We then add an N/10 (in case the chlorine content is extremely feeble N/100) solution of silver nitrate in excess and 2 cc. of an iron-alum solution[1]), after which we extract with ether. As soon as the ether has separated again, the watery layer is withdrawn and the excess of silver nitrate titrated back with a N/10 or a N/100 solution of ammonium sulphocyanide, as the case may be.

Of strongly chlorinous benzaldehydes only 10 g. need be used, when of course all the other quantities indicated must be reduced to half. It is easy to estimate roughly the chlorine content by the qualitative test (combustion method)[2]).

The following values were established by this method for mixtures of known chlorine content: —

Benzaldehyde	+ 0.1	p.c.	Cl	(added	in	form	of	benzyl	chloride)	found	0.096	p.c.	Cl
„	+ 0.05	p.c.	„	(„	„	„	„	„	„)	„	0.045	p.c.	„
„	+ 0.02	p.c.	„	(„	„	„	„	„	„)	„	0.0185	p.c.	„
„	+ 0.01	p.c.	„	(„	„	„	„	„	„)	„	0.009	p.c.	„

This shows that the results obtained are quite satisfactory, but the process is after all rather complicated, which has all the more weight, as it does not permit of determining the chlorine in the nucleus, as stated before, upon which everything here depends. Furthermore, there is the other drawback, that it may easily give rise to differences between seller and buyer, when the chlorine content is guaranteed. We had a little foretaste thereof, when we procured for ourselves three samples with guaranteed content of chlorine. Only in one case the quantity of chlorine determined by above method tallied with that indicated, whereas in the two other cases there were rather considerable differences: —

Benzaldehyde	I.	guaranteed	to	contain	0.2,	found	0,41 per cent.
„	II.	„	„	„	0.08,	„	0,087 „ „
„	III.	„	„	„	0.02,	„	0,081 „ „

It is almost the same with Vaubel's test (heating the benzaldehyde with concentrated sulphuric acid. Comp. *Report* April/October 1918, 61), which M. S. Salamon recommends as useful. Only the chlorine of the side chain can be determined with it.

As matters now stand, we are of opinion that it is worth considering, whether it would not be better to adhere to the former stand-point, according to which a benzaldehyde is either free from chlorine, or not. If the article free from chlorine is extremely scarce at present, it is a sad sign of the times we are living in, but we must hope for better ones. The essential question is after all, whether chlorine is present, or not, and whether there is a little more or less, comes second. As long as there is no really reliable method, the quantitative test ought to be restricted to where it is absolutely necessary, whereas in other cases one should take as a criterion the result of the qualitative chlorine test according to the combustion method. If the prescription is strictly adhered to, this test permits of forming a judgment, whether the

[1]) The iron-alum solution must not be added after the extraction, as there would again be a precipitation. It is a solution of iron-alum in water, saturated in the cold, to which concentrated nitric acid has been added until it is colourless. The nitric acid must be free from nitrogen oxides, as these would disturb when titrating back with a solution of ammonium sulphocyanide. They are eliminated by boiling. — [2]) *Report* October 1911, 119; Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 609.

benzaldehyde contains more or less chlorinated compounds, which will be quite sufficient for business purposes in most cases. We consider a benzaldehyde as poor in chlorine, if the aqueous test solution, to which silver nitrate has been added, only shows a very feeble, just perceptible opalescence, which corresponds to a content of about 0.02 per cent. of chlorine. The reaction becomes more intense with increasing chlorine content; when it is 0.03 per cent., for instance, there is a milky turbidity.

Our studies of the quantitative determination of chlorine in benzaldehyde are still going on, so that we shall revert to the subject in our next *Report*.

Several years ago, W. Denis and P. B. Dunbar[1]) described a method of determining benzaldehyde by means of phenylhydrazin. Geiger[2]) obtained good results with it, after having slightly modified it. He is of opinion, however, that benzaldehyde should not be used for verifying the method, as it is practically impossible to protect the aldehyde against oxidation. The bisulphite compound, on the contrary, is fairly stable and can be weighed without any fear of oxidation. On addition of dilute sodium lye, it yields benzaldehyde quantitatively. In order to prepare the bisulphite compound, Geiger adds a saturated sodium bisulphite solution to the benzaldehyde, washes the resulting compound with 95 per cent. alcohol, crystallizes it twice from 50 per cent. alcohol and dries it in the exsiccator over sulphuric acid or soda-lime. Combustion confirmed the formula C_7H_6O, $NaHSO_3 + {}^1/_2H_2O$, indicated by Bertagnini. Geiger tests mixtures of benzaldehyde and benzoic acid as follows: he adds sodium lye to the mixture until the reaction is distinctly alkaline, extracts it three times consecutively with 25 g. of ether in each case. To the ethereal extract he adds 1.5 cc. of freshly distilled phenylhydrazin[3]) and 10 cc. of a 10 per cent. ethereal solution of acetic acid and then evaporates the ether in a current of air. The residue is composed of benzalphenylhydrazone[4]), phenylhydrazin acetate and acetic acid. After having mixed it with about 50 cc. of water and allowed to stand for 5 or 10 minutes, it is filtered through a weighed Gooch crucible, dried for two hours in a vacuum at 70° and weighed.

The liquid obtained through extraction with ether is acidulated with hydrochloric acid (1:1), extracted once with chloroform, then saturated with common salt and shaken three times consecutively with 25 cc. of chloroform in each case. The collected chloroform extracts are evaporated to dryness in a current of air at room temperature, the remaining benzoic acid being dissolved in 50 per cent. alcohol and titrated with phenol- or thymolsulphonphthalein[5]) as indicator.

Mixtures of benzoic acid and benzaldehyde-sodium bisulphite were analysed in this way, when very exact results were obtained.

As to the preparation of benzaldehyde cyanhydrin see page 17 of this *Report*.

Benzyl alcohol. According to an Australian medical paper[6]), benzyl alcohol belongs to the modern local anæsthetics and is supposed to be a valuable substitute for cocaine. A one per cent. solution of benzyl alcohol in water proved to be a good anæsthetic for opening abscesses, tearing out toe nails and other operations.

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[1]) *Journ. Industr. and Engin. Chemistry* **1** (1909), 256; *Report* October **1909**, 155. — [2]) *Journ. Americ. Chem. Soc.* **40** (1918), 1453. — [3]) Geiger recommends to distil the phenylhydrazin in a current of hydrogen and to keep it in a hydrogen atmosphere. — [4]) The presence of small quantities of benzyl alcohol does not interfere. It is extracted with the benzaldehyde and can be separated from the benzalphenylhydrazone through washing with 10 per cent. alcohol. — [5]) See also page 75 of this *Report*. — [6]) The *Medical Journal of Australia* of 3rd August **1918**; *The Chemist and Druggist of Australasia*, January **1919**. As per the *American Journ. Pharm.* **91** (1919), 297.

Copaiba Balsam. As to Columbia copaiba balsam, see page 20 of this *Report*.

Coumarin. H. J. Wichmann[1]) has worked out the following method for detecting and determining coumarin in artificial extracts of vanilla: 10 cc. of the extract are made alkaline with 10 per cent. soda lye, diluted with 16 cc. of water and extracted with 20 cc. of ether. In case the ethereal extract is feebly coloured, it is shaken with some cc. of concentrated alcoholic potash lye and washed with 19 cc. of water, thus eliminating all organic acids, vanillin, colouring matter or saccharin. Then 1 cc. of 50 per cent. potassium hydroxide solution is added to the ethereal liquid and after the ether has been evaporated the residue is melted over an open flame. If coumarin is present, there is a greenish-yellow flame when the melting begins, but which suddenly disappears on further heating, a sign of the coumarin having been converted into salicylate. The melted substance is dissolved in a few cc. of water, acidulated with sulphuric acid and extracted with 5 to 10 cc. of benzene. Benzene is to be preferred to other solvents because of its lesser density, its lesser dissolving power for mineral acids and because protocatechuic acid, which is formed out of the vanillin that may have been dissolved in the ether, is insoluble in it. The benzene solution is washed with a little water, filtered and tested with 1 or 2 cc. of dilute ferric chloride solution for salicylic acid. If there is no turbidity, one neutralizes with N/10 soda lye the traces of mineral acid that might prevent the colouring.

In order to determine quantitatively the coumarin in vanilla extracts, 50 cc. of the extract are treated with lead acetate, without removing the alcohol. One then fills up to 100 cc., filtrates and precipitates the excess of lead with dry potash oxalate. 50 cc. of the filtrate thereof are extracted with ether, benzene or chloroform. In order to free the extract from the vanillin, a small quantity of phenolphtalein solution is added and alcoholic potash lye in excess. Then it is washed several times with 10 cc. of water in each case, until the red colour disappears. The washed solution, which contains the coumarin, is evaporated and the residue dried and weighed.

Eucalyptole. Generally speaking terpene-like bodies are sparingly soluble in water, which is the case too with eucalyptole (cineole). J. C. Earle[2]) determined the solubility of this oxide in water. He found that

at	1,5°	0,64 g.	cineole	dissolve	in	100 g. water
„	7,5°	0,57 g.	„	„	„	100 g. „
„	10°	0,54 g.	„	„	„	100 g. „
„	21°	0,35 g.	„	„	„	100 g. „
„	40°	0,21 g.	„	„	„	100 g. „
„	50°	0,19 g.	„	„	„	100 g. „

According to these figures the solubility of cineole would decrease with rising temperature.

The same author reports on the sensitiveness of the well-known iodole method for proving the presence of cineole. He heated 1 cc. of cineole with varying quantities of phellandrene and with iodole in a testing tube and filtrated the mixture on to a watch glass. With a dilution of 1 part of cineole in 3 parts of phellandrene, the iodole double compound separated immediately, with a proportion of 1:10 after a short while and with a proportion of 1:20 or 30 after half an hour.

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[1]) *Journ. Industr. and Engin. Chemistry* **10** (1918), 535; *Chem. Zentralbl.* **1918**, II. 1087. — [2]) *Journ. Soc. chem. Industry* **37** (1918), 274 T.

C. E. Fawsitt and C. H. Fischer[1]) report on the use of cineole as a solvent in cryoscopy. They indicate as melting point of the cineole +0.9°, being of opinion that the usual indication of —1° is due to the presence of water in the ordinary product[2]). Cineole cannot generally be used as a cryoscopic solvent owing to its being hygroscopic. In certain cases, however, it would be preferable to benzene, although it is more difficult to work with cineole. The cryoscopic constant is 6.7, the latent heat of melting 22.2 calories per gram.

On page 62 of our *Report* of October 1918, we discussed a communication by R. B. Krauss and E. Crede[3]) on the use of chlorinated eucalyptole as a solvent for dichloramin-T. This solvent has so many drawbacks, however, that it had to be replaced by another, "chlorocosan", obtained through conducting chlorine gas into melted paraffin at from 125 to 140°, as we cull from a publication by E. Fullerton[4]).

A 10 per cent. solution of dichloramin-T in chlorinated eucalyptole, if stored in an absolutely dry state in yellow bottles away from the light, keeps, it is true, for a month or longer, under favourable circumstances, but if the solution is filled into a damp flask or is exposed to the light for a short while, it decomposes quickly and a precipitate of p-toluenesulphonamide is formed with liberation of chlorine. The solution thus becomes strongly irritating. Even under favourable circumstances, excluded from moisture and light, the dilute solution decomposes quickly, so that is was recommended never to use dilute solutions more than 24 hours after their preparation and to remove from the vessels and other implements all traces of the old solution with the aid of chloroform or carbon tetrachloride.

Frankincense. The Journal of Commerce of 12th June 1918[5]) relates the following out of a consular report on the trade of the Aden district: Some of the most important natural products of Aden are frankincense, myrrh and gum arabic. In 1916/17 the market and the prices for these articles were quite satisfactory. Although the quantities put on the market were smaller than in the previous year, the total value rose. Aden is supplied with frankincense almost exclusively by the free Somali ports and the Arabian gold ports. This resin belongs to the chief kinds of resin of the local market. Most of it is exported to India. The quantities sent there in 1916/17 have not been exceeded in any previous year. The exports to France have increased likewise, whereas those to Abyssinia dropped and nothing was exported to Egypt, which used to take considerable quantities. This aromatic resin is chiefly used in the countries referred to in religious ceremonies and for disinfection. Nothing was exported to the United States. Myrrh comes next in importance. It is chiefly imported from the free Somali ports. In 1916/17 the largest quantities were exported to Egypt, India and the United States, the last-named countries taking almost three times as much as in the previous years. It seems that a permanent trade is developing in this direction.

Ionone. We have repeatedly pointed out in this *Report*, that the phthalic ester, frequently used as a basis for perfumes without alcohol, began last year to act an important part in the adulteration of other oils (comp. pages 15, 38, 67). Among the products offered by the Leipzig firm in question is a so-called "Oil of Violets

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[1]) *Journ. Royal Soc.* of N. S. W. **51** (1918), 467; *Journ. chem. Soc.* **114** (1918), II, 257. — [2]) We think more of impurities of other kinds. We have observed a m.p. of +1 to +1.5° with goodpreparations of our own. — [3]) *Journ. Americ. chem Soc.* **39** (1917), 2720. — *Americ. Journ. Pharm.* **90** (1918), 16. — [4]) *Americ. Journ. Pharm.* **90** (1918), 629. — [5]) *Nachr. f. Hand., Ind. u. Landw.* **1918**, No. 124, p. 3.

100 per cent.", a sample of which was sent us from Hamburg for inspection. The excessive specific weight ($d_{15°}$ 1.0809) aroused suspicion at once, as well as the fact that it dissolved already in 1 vol. of alcohol 70 per cent., whereas oil of violets requires 2.5 to 3 vols. 70 per cent. alcohol for dissolving and has a specific gravity of from 9.935 to 9.94. The saponification supplied at once the explanation for the irregularities. Pure oil of violets, as is well known, does not contain any saponifiable constituents, wheres here an acid v. of 2.8 and an ester v. of 436.8 were stated. The acid separated from the saponification lye was identified as phthalic acid by its m. p. of 197°. The content of dimethyl phthalate calculated from the ester v. amounted to 75.5 per cent., so that this "100 per cent." oil of violets consisted in reality mostly of another compound. One cannot deny said firm a certain thoroughness, but it is unfortunately misplaced and worthy of a better cause. Taking into consideration the present high prices for everything, such manœuvres will certainly pay well.

Menthol. The Japanese export figures for menthol for the first six months of the three last years are as follows[1]): —

	1917	1918	1919
British-India	5620	10809	3946
Great Britain	17241	100801	23006
United States	110096	42621	110373
Other countries	10175	7384	4107
kin:	143132	161615	141432
to the value of yen:	932754	977882	1400675.

A solution of 2 parts of menthol, 2 parts of phenol and 1 part of eugenol has been included in the last edition of the Swedish Pharmacopœia under the name of *Tinctura antiodontalgica*, owing to the action of menthol as a local anæsthetic, for which it is sometimes used in dental surgery. Now a method for determining the menthol content is required for the State control of this preparation. The usual acetylation cannot be taken into consideration, as O. von Friedrichs[2]) correctly observes, owing to the presence of eugenol and phenol, nor the formic acid method, introduced by Simmons[3]). The simplest would be to determine the menthol content with the aid of specific rotation. If this is calculated from the rotation found, it results that the variation of the percentages in the various solvents causes a modification of the specific rotation, *i. e.* a decrease with rising content of the optically active body, such as is the case with most of the active substances. A modification of the solvent likewise brings about a change in the specific rotation, when the addition of eugenol raises the rotation.

Von Friedrichs examined 10 to 50 per cent. solutions of menthol in eugenol, 25 to 50 per cent. solutions in phenol and three series of 10 to 50 per cent. solutions in phenole and eugenol, in which the proportions of the two inactive bodies were 2:1, 1:1 and 1:2, respectively. For solutions in only phenol, 25 per cent. has been chosen as the lowest menthol content, as similar preparations made in the warmth and containing 20 per cent. of menthol or less do not keep liquid when cooling down to room temperature. The rotations were measured and the specific gravities determinedat + 18°.

It results from the tables contained in the original that the angle of rotation of the menthol in phenol solution is not far from a linear function of the concentration.

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[1]) *Chemist and Druggist* **91** (1919), 1105. — [2]) *Arch. der Pharm.* **257** (1919), 72. — [3]) *Analyst* **40** (1915), 491; *Report* October **1916**, 89.

According to the values found by the author for α_D and d, the percentage p may be expressed by the following equation, whenever no great accuracy is required: —

$$p = -\frac{2.153 \cdot \alpha}{d \cdot l}.$$

The summary in the original permits of calculating the direct relation between p and α by the method of the smallest squares, which is more appropriate for exact investigations. One then obtains

$$p = -1.924\,\alpha + 0.01207\,\alpha^2.$$

The conformity of the values observed for p with those calculated according to these formulæ is explained by another summary in the original. The difference for the solution in question varies between — 0.03 and + 0.16 per cent.

For solutions of menthol in a mixture of 2 parts of phenol and 1 part of eugenol, the relations are as follows: —

$$p = -\frac{2.115 \cdot \alpha}{d \cdot l}$$

or

$$p = -1.9224\,\alpha + 0.01023\,\alpha^2.$$

For a solution of menthol in an equal quantity of eugenol the values are: —

$$p = -\frac{2.108\,\alpha}{d \cdot l}$$

and

$$p = -1.9215\,\alpha + 0.01001\,\alpha^2.$$

For menthol in phenol and eugenol (1 + 2) the values are: —

$$p = -\frac{2.1026 \cdot \alpha}{d \cdot l}$$

and

$$p = -1.914\,\alpha + 0.01023\,\alpha^2.$$

For solutions of menthol in eugenol[1]) the relations are: —

$$p = -\frac{2.0955 \cdot \alpha}{d \cdot l}$$

and

$$p = -1.9017\,\alpha + 0.01063\,\alpha^2.$$

Finally, von Friedrichs reports on the calculation of the true specific rotation of the menthol. If the variability of the specific rotatory power is represented as a function of the percentage of inactive substance, there are no straight lines obtained in the net of coordinates, but curves which are a little more accentuated for the solutions in phenol than for those in eugenol. The attempts to infer the true rotatory power of the menthol from the increase of the specific rotation with the content of phenol or eugenol, respectively, according to the general formula

$$[\alpha]_D = A + Bq + Cq^2$$

have led to the following equations, the first of which also permits of calculating the rotations of such phenol solutions as do not occur in the liquid state at 18°.

One finds for solutions in phenol

$$[\alpha]_D = -48.24 + 0.0827\,q - 0.000889\,q^2$$

and for solutions in eugenol

$$[\alpha]_D = -48.75 + 0.0536\,q - 0.00061\,q^2.$$

[1]) 1 + 2?

Oenanthol. For the reduction of aldehydes to the corresponding alcohols, P. A. Levene and F. A. Taylor[1]) recommend the use of an emulsion of metallic sodium in toluene. They suspend the calculated quantity of sodium in dry toluene, heat until the metal melts, shake vigorously and cool quickly with ice under continuous shaking. They then add to the emulsion the aldehyde, dissolved in glacial acetic acid and toluene, and, as soon as the reaction is complete, some water for dissolving the sodium acetate, separate the toluene from the aqueous solution and fractionate. The yield of heptyl alcohol was 58 per cent. of the theoretic quantity; b. p. 175.5 to 176.5°; urethane, m. p. 60°.

Pollantin. On page 65 of our *Report* of October 1918, we discussed F.W. Heyl's[2]) publication on the chemical composition of the pollen of *Ambrosia artemisifolia*, L., *Compositæ*. This pollen as well as that of *Ambrosia trifida* has been investigated by J. H. Koessler[3]), in order to find out whether the chemical composition would afford any clue as to the toxic action causing hay-fever. The contents in 100 parts were: 10.5 parts of water, 10.6 parts of ashes, 6.89 parts of sugar (after hydrolysis), 10.3 parts of lipoids soluble in ether, 4.75 parts of fatty acids (after saponification), 0.34 part of phytosterol, 12.5 parts of constituents soluble in alcohol 95 per cent., 11.5 parts of extractive matter soluble in alcohol and water and 37.71 per cent. of insoluble residue. The hydrolysis of the albumen, calculated for the pollen, gave the following figures: 2.13 per cent. arginine, 2.41 per cent. histidine, 0.57 per cent. cystine and 0.97 per cent. lysine.

Koessler is inclined to attach great importance to the comparatively high content of histidine, owing to its relation with the poisonous imidazolylethylamine.

Saffron. In the communication no. 37 of the Committee for fostering the cultivation of medicinal plants in Austria by the Government[4]), R. Kuráž deals with the growing of saffron, which according to his opinion is one of the useful plants, to which the Austrian agriculture will have to show more attention.

The cultivation of saffron is now scarcely to be found at all in Lower Austria, except in Maissau, where the production is so small, however, that Austrian saffron is without any importance for the world's trade. At present the Spanish saffron cultivation is the most considerable, and its production has a decisive influence on the world's market.

The consumption of saffron being very considerable in Austria-Hungary, large sums are paid to foreign countries for this condiment. From 1910 to 1913, Austria-Hungary imported 86200 kilos of it to the value of 8738470 crowns. For this reason the author thought it worth while to recall the leading facts about the cultivation of saffron. It is specially recommendable to small farmers with big families, the members of which can then do all the work connected with it, above all the collecting, which takes a great deal of time. Saffron growing affords excellent occupation without any over-exertion to older children.

As even a short summary of Kuráž's notes would require too much space, we wish to call attention only to some of the most important points.

True saffron can be cultivated with success in all the wine-districts. It requires dry and very hot weather in July and August and warm, fine days especially during

[1]) *J. Biol. Chem.* **35** (1918), 281; *Journ. Soc. Chem. Industry* **37** (1918), A. 606. — *Chem. Zentralbl.* **1919**, I. 349.
[2]) *Journ. Americ. Chem. Soc.* **39** (1917), 1470. — [3]) *Journ. Biol. Chem.* **35** (1918), 415; *Chem. Zentralbl.* **1919**, I. 393. — [4]) After a reprint kindly sent us.

the flowering season, from end of September to the middle of October. The plant stands the cold temperature in winter quite well. The best soil for saffron is a light, dry, loose and well-aired sandy clay, which does not form crusts and has been carefully looked after.

It is planted in beds (saffron gardens), where it remains for several years in one place. The cultivation may be carried on in a garden (small scale) or on fields, generally after cereals.

The cultivated saffron *(Crocus sativus,* L., var. *culta autumnalis; Iridaceæ)* is looked upon as a variety due to crossing. It is propagated exclusively by the bulbs, as there are never seeds. The bulbs are planted in the last week of August or the first week of September. Sometimes it is recommended to do it already in July. A ditch of moderate depth is drawn round the plantation. If saffron is grown on a field, a good fence is necessary, in order to keep the cattle out of the way and also the hares, which are very fond of saffron leaves.

About 4 weeks after planting, *i. e.* end of September or beginning of October, the flower rises direct from the bulb, exhaling a feeble violet odour. The gathering begins as soon as the first flowers show. It is better not to collect on rainy days. After the crop and during the winter the saffron beds or fields require no care at all, but a removal to another site is generally necessary every three or four years. Some growers, however, think it preferable to wait five or six years, as all kinds of crocus increase their production of flowers from the third year to the sixth.

The natural enemies of saffron are especially game, cattle, sheep and goats. Pigs also like to dig up the bulbs. Sometimes mice cause a good deal of damage through gnawing the bulbs and moles are also unwelcome guests in saffron beds. The most dangerous fungus pest is *Rhizoctonia crocorum,* DC., which is noticed sometimes in summer to such an extent, that the whole cultivation has to be abandoned. Remedies against it are carbon disulphide and formaldehyde.

As to the yield of saffron stigmas, the records vary considerably. In the first year about 30 to 60 grams are to be expected per are (100 qm.), the total for three years, in Lower Austria, being indicated as between 190 and 325 grams. In England, about 500 grams are said to be collected in a similar period; according to other versions, about 25 grams in the first, 136 grams in the second and a little more in the third year. The figures given for France are somewhat more favourable. The numbers of flowers required for the production of 1 kilo of dry saffron oscillate between 80000 and 350000, according to the weather conditions and the amount of pistil left on the stigma.

According to Schmalhausen, *Crocus Pallasi,* closely allied to the cultivated variety and yielding a condiment of strong, characteristic smell and excellent quality, occurs in Dalmatia. It comes up to the best genuine article, from which it cannot be distinguished.

Storax, American. An American periodical contains a treatise by F. E. Watermeyer[1]) of the firm of Fritzsche Brothers, New York, of which the following is a copy, unfortunately without the two illustrations.

High up in the mountains of Honduras in Central America are vast forests of the species *Liquidambar Styraciflua,* L., called the American Styrax or Storax tree, its valuable secretions being known among the Mexicans and Creoles as *Copalme.* The accompanying pictures illustrate a section of the trunk of one of these trees

[1]) *Americ. Perfumer* **14** (1919), 161.

from eight to ten years old, also the leaves, which are three-pointed when young and five-pointed when matured. The leaf colour changes according to the season, in winter being pronouncedly green and in summer of a purple hue. As the tree blooms only in winter, it was impossible to include the flowers, as these specimens were collected in the summer.

Shortly after the discovery of America, the fragrant balsam of the American Styrax tree became celebrated throughout Europe. Its praises were sung by Monardes, and it was used as a source of supply by the Old World for perfume, incense, ointment and medicine. Whole shiploads were sent from Mexico to Spain and so widely was it used that early writings state that the odour permeated the atmosphere of whole towns and villages. Its use has declined considerably during the past century, possibly owing to the difficulty experienced in its collection and to the wider distribution of manufactured perfumes.

For many years now its Old World prototype, liquid gum styrax of Asiatic origin, from *Liquidambar Orientalis*, L., has formed the chief source of supply for the entire world. With the beginning of the World War and the accompanying scarcity of imported materials, it became exceedingly scarce and a large portion of the supplies that found their way to these shores were of inferior quality, having been deprived of some of their natural aromatic constituents. As the balsam is a valuable perfume material for soaps as well as toilet preparations in general and is an important ingredient of many pharmaceutical preparations, it became necessary to turn to our own resources for a future supply.

Although this tree is widely distributed throughout our southern states and its product, the so-called "sweet gum", has been long and favourably known, the scarcity and high cost of labour during the past four years made it impossible to utilize this source except for small and unimportant parcels. In Honduras, however, were found present all those conditions of labour and adequate natural ressources most favourable for the collection of the balsam on a large scale and it is from this source, therefore, that our domestic manufacturers have indirectly obtained their supplies of the American gum for the past three or four years.

Unfortunately, these Honduran forests are exceedingly difficult of access, and the difficulties attendant upon the collection of the gum are so great that only the poorest natives can be induced to engage in the enterprise. The cost, accordingly, is somewhat higher than formerly prevailed for the Asiatic grade, but consolation exists in the fact that this product of our own continent is richer in aromatic constituents, and, in general, superior in quality to any offered here prior to the war.

On the section of bark illustrated is seen a slight excrescence which, in time, develops into a pocket in which the balsam is secreted. When these pockets are located near the basis it is unnecessary to destroy the tree, but many are high up, in which case the tree must be felled. The labourers generally work in groups of four and a full day is frequently required to bring down one well matured tree. On an average, not more than one tree in every one hundred square yards will be found worthy of attention, the others not containing balsam, due to age or other conditions of growth. The balsam-bearing tree is easily recognized by the excrescence above mentioned, but it requires an expert in the business to judge from the outward appearance if the pocket actually has any balsam in it. The pockets contain from one to four bottles, the bottles holding about 2 lbs. each.

Once the tree is felled, a cut is made in the excrescence and, as in the collection of the sap of the rubber tree, a small gutter inserted, the free end leading into a con-

tainer. The liquid is thick and flows slowly. When the container is filled the contents are emptied into a larger one, generally of a capacity of about 25 bottles or 50 lb.

The most difficult part of the operation is now to get the balsam out to civilization and this can only be accomplished by transporting these 50 lb. containers on the shoulders of the natives. Frequently they must be carried ten to twelve miles before a point is reached, whence the remainder of the journey can be made on muleback. The country thereabout is primitive, of rugged topography, no roads exist, and violent and sudden rainstorms add to the dangers and difficulties of those engaged in the enterprise. Not infrequently a mule with native and styrax goes to destruction over a precipice, entailing considerable financial loss upon the manager of the expedition. In general, it may be correctly said that the collection of this balsam forms about the hardest task the natives are ever called upon to perform.

Unfortunately, the trees which have been felled represent an economic loss, as there is no way of utilizing the lumber at its source nor bringing it down to civilization. As yet, no attempt has been made at reforestation, and since centuries are required to produce the deposits it is conceivable that the supply will eventually become exhausted unless new sources are discovered.

While Asiatic styrax may again be freely available with the resumption of normal conditions of import, so much more valuable has the American product proved that for some purposes it will probably continue to be preferred and should be an important factor at least in forcing the exporter of the Asiatic gum to maintain a better uniform quality than in the past. The following is an analysis of an average sample of the American liquid styrax: Incineration residue = traces only, purified balsam = 85 per cent., sap. v. = 179, acid v. = 41.

It will be noticed that the content of cinnamic acid is abnormally low, which indicates a correspondingly higher content of natural aromatic constituents, since the acid is a product of decomposition at the expense of those ingredients upon which the value of the balsam primarily depends. While the American product is not official, its higher quality has earned for it at least a place alongside of, and a title equal to, that of the Asiatic product, and it will serve, moreover, to make the American consumer independent of a foreign source of supply, should similar chaotic conditions ever again confront us.

On page 75 of our April/October *Report* **1916**, we discussed a treatise of M. Henze[1]), containing the surprising news, that he had proved the presence of *d*-primaric and abietinic acids in storax gum. L. van Itallie and H. J. Lemkes[2]), however, could not find these two acids in pure products and presume, what we think to be correct, that Henze examined an adulterated article. He[3]) now examined a guaranteed pure gum storax and again proved the presence of abietinic acid to an extent of about 30 per cent.

A. Tschirch[4]) nevertheless quite supports the views of van Itallie and Lemkes, taking it that Henze investigated an adulterated product. As Tschirch and Henze's publications are of a somewhat polemic nature, we barely mention the fact, adding only that Tschirch calls attention to K. Dieterich's verdict in his *Analyse der Harze* (analysis of resins), where all commercial qualities of storax are declared to be adulterated. According to Tschirch, storax is faked mostly with balsams from conifers.

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[1]) *Berl. Berichte* **49** (1916), 162. — [2]) *Pharm. Weekblad* **55** (1918), 142; *Report* April/October **1918**, 66. — [3]) *Schweiz. Apotheker-Ztg.* **57** (1919), 351. — [4]) *Ibidem* 355.

Terpineol. A. Joure[1]) made an observation regarding the storing of chloroform for narcosis, which may be very valuable but strongly requires verification. He found that the inactive terpineol has the property of protecting chloroform against physical and chemical influences (light, oxygen, water) which may bring about changes in its composition. No decomposition products could be found in pure chloroform containing less than 1 per cent. of terpineol. Their formation had either been prevented altogether, or they had combined with the terpineol. The chloroform remained stable, even if stored under the most unfavourable conditions, *e. g.* in unstained bottles, in bottles only partly filled and even in the presence of water.

Thymol. *Monarda punctata.* L., a labiate, belongs to the plants that might be used with success for the manufacture of thymol. It has been tried already to cultivate it in the United States[2]) and in Montserrat[3]). The oil, distilled from the (green?) leaves with a yield of 9.27 per cent., was of lemon-yellow colour and had the following properties: $d_{16.5°}^{39°}$ 0.928, α_D — 1° 66′(?!), $n_{D28°}$ 1.501. It contained 60.4 per cent. phenols, from which 44 per cent. of crystallized thymol could be separated.

Ajowan oils, distilled from seed also grown in Montserrat (yield 2.7 to 3.1 per cent. of air-dried seed), showed the following constants: $d_{16.5°}^{39°}$ 0.9112 and $d_{15°}$ 0.925, α_D 1° 66′(?!) and + 0.90°, phenol content 47.3 per cent., thymol content 43.5 and 54 per cent. An oil from St. Kitts showed $d_{16.5°}^{39°}$ 0.922 and a phenol content of 53 per cent. The optical rotation could not be determined, owing to the dark colour of the oil.

As to further trials of growing ajowan in the Seychelles and Montserrat, see page 5 of this *Report*.

Some time ago, in a publication on the sulphonephthalein ranges of indicators and the quinone phenolate theory, H. A. Lubs and S. F. Acree[4]) described among other subjects the preparation of thymol sulphonephthalein. This body is obtained on melting for four hours a mixture of thymol, sulphobenzoic acid chloride and zinc chloride at 140° and under frequent stirring. After recrystallization from alcohol, the thymol sulphonephthalein forms greenish crystals. Its very dilute acid solutions are yellowish, the concentrated ones reddish, whereas the basic solutions are deep blue in the reflected and deep red in the transmitted light. Three to six drops of a 0.04 per cent. alcoholic solution give, according to A. B. Clark and H. A. Lubs[5]), a good indicator for acidimetric and alkalimetric titrations. They mention as examples the titrations of mixtures of benzoic and hydrochloric acids, acetic and hydrochloric acids, acetic and sulphuric acids and of aniline with hydrochloric acid. It is true, the titration is possible only with certain concentrations, further relative particulars being given in the original.

W. Zinn[6]) mentions that thymol is praised from various quarters as a remedy against trichinosis. It is given in doses of 0.5 g. every two or three hours.

Vanillin. Adulterations of vanillin with antifebrine, formerly observed repeatedly, have now become very scarce. A sample received from Hamburg proved, however,

[1]) *Rép. de Pharm.*; *Pharm. Weekblad* **56** (1919), 189. As per *Apotheker-Ztg.* **34** (1919), 76. — [2]) Comp. S. C. Hood, Bulletin No. 372 of the U. S. Dep. of Agric.; *Report* October **1917**, 100. — [3]) *Perfum. Record* **10** (1919), 19. — [4]) *Journ. Americ. Chem. Soc.* **38** (1916), 2772; *Chem. Zentralbl.* **1917**, I. 813. — [5]) *Journ. Americ. Chem. Soc.* **40** (1918), 1443. — [6]) *Therapie der Gegenwart* **1919**, 81; *Therap. Monatsh.* **33** (1919), 233.

that they do not entirely belong to the past. It melted already between 62 and 66°, instead of between 80 and 82°, which fact roused suspicion at once. On further investigation, it resulted that the product had been adulterated with 20 to 25 per cent. of antifebrine. The separated admixture was recognized as antifebrine by its m. p. of 114° and by its isonitrile reaction. The purified vanillin then melted at 81°.

It may be taken as a well-known fact that vanillin is widely spread in nature; it has been found of late even in arable soil (see page 146). The potato is one of the plants in which it occurs, the layers next to the peel tasting distinctly of vanillin, sometimes. But also the flowers of the potato plant, although they generally do not smell at all of vanillin and only occasionally quite faintly, may contain quite appreciable quantities of this body, according to E. O. v. Lippmann[1]). He noticed for instance that the beautifully blue flowers (but not the white ones) of potato plants grown near Kissingen exhaled a surprisingly strong vanilla perfume, which was purest and strongest in the early morning but disappeared completely after insolation for some time. The picked flowers likewise lost their smell very soon. It was possible to prepare, with the aid of ether, an extract smelling of vanilla, from which vanillin was isolated by means of its bisuphitic compound. The regenerated vanillin melted at 81° and sublimed unaltered. With ferric chloride it gave the characteristic blue colouring.

A communication on vanilla growing in Java, taken from an official Dutch periodical[2]), reads about as follows:

Vanilla introduced from Mexico was first cultivated in Java about the middle of the 19th century. Already after a very short time, considerable profits were made with this new branch of cultivation, but the prices soon declined[3]) owing to the vigorous competition of the artificial vanillin.

Nevertheless vanilla growing has been maintained in Java and is still considered very lucrative. The net profits sometimes amount to 1000 guilders per bouw[4]) in normal years.

A vanilla plantation begins to bear in the third year. As cultivation and curing require numerous skilled hands, natives do not come into consideration for the work and only small vanilla farms can prosper. In the Preanger district, a plantation of ten years standing yielded from 200 to 500 lbs. of vanilla beans per bouw. Vanilla requires a sandy soil rich in humus with permeable sub-soil and thrives best in districts with really dry monsoon and an average temperature of 25°. In Java (Garut), it requires an elevation of 2000 feet above sea-level. The decayed leaves of the trees grown for shading or supporting the vanilla plants, mould from stable-dung and Chili saltpetre serve as manure. Straight beans being asked for in commerce, one prefers to fertilize only the largest flowers, situated at the lower end of the racemes. In Java, more value is generally attached to a large yield than to excellent quality. The best vanilla beans are those collected immediately after maturity, *i. e.* 6 to 9 months after fertilization.

In Java, the beans are treated as follows: the ripe fruits are dipped into boiling water for about two minutes, then rubbed between flannel and dried in a current of air. The beans thus obtained are 15 to 25 cm. long and dark brown or black in colour. They are pulled straight between the fingers and finally sorted, when due attention must

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[1]) *Berl. Berichte* **52** (1919), 905. — [2]) *Handelsberichten (Den Haag)* **12** (1918), 374. — [3]) We would remark that this cannot be the case, as vanillin was first put on the market in 1875 and was then very dear. Some time afterwards it became cheaper. — [4]) 1 bouw = about 7100 sq. m.

be given to form, aroma, brilliancy and an uninjured, fatty surface without any spots. The packing is of great interest from a commercial point of view, as the appearance is the chief criterion, however good the aroma otherwise may be. The grower is very careful in sorting and packing, as well as in combining the bundles; the straight beans are in the centre, then come the curved ones, and the most beautiful are on the outside. The bundles are tied with raffia at both ends and in the middle and then packed in tins of from 10 to 12 kilos, on which the trade-mark and the quality are indicated. Three such tins are put in a wooden box, thus containing from 30 to 36 kilos. Storing in glass-stoppered bottles or wrapping up in tinfoil, fosters the development of the aroma.

The exports from Java and Madura were (in kilos): —

Destination	1913	1914	1915	1916
Holland	1420	2200	251	105
United States	492	804	489	593
Great Britain	350	178	—	—
France	102	—	—	—
Other countries	93	45	37	50
Total	2457	3227	777	748

The world's production of vanilla amounts to about 500000 kilos.

In a Dutch colonial paper[1]) we find a note on vanilla, which may be of interest for our readers. It is difficult to say just now, whether the views therein exposed are correct, but the author seems to be rather pessimistic with regard to the prospects of vanilla growing.

According to him, vanilla is a product that, owing to the war, has almost disappeared from the world's market the reasons being: lack of hands, increasing difficulties of transport and the fact that vanilla is not an indispensible food-stuff. All the belligerent countries have, little by little, ceased to import this condiment. There is still a little trade, but under difficulties, with some neutral countries, such as Switzerland, Scandinavia and Holland. Since the article has been commandeered by the United States Government, the export from France has been prohibited. The consumption in France is decreasing steadily, as the manufacture of chocolate and confectionery seems doomed to disappear more and more. In consequence of this unfavourable state of affairs, the prices in the colonies have dropped from 18 and 20 to 12 Francs per kilo. Although this price did not pay, it was to be hoped that some growers would be able to maintain their plantations in spite of the difficulties and losses during the years of war, as a vanilla plantation once abandoned could not be brought back into working order within a year.

The vanilla exports from the Seychelles in 1917 are to be valued at 50837 Rupees, as compared with 164069 Rupees in 1916[2]).

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[1]) *Indische Mercuur* of 5th July 1918; *Journal d'Agriculture tropicale.* — As per *Nachr. f. Handel, Ind. u. Landw.* **1918**, No. 105, page 2. — [2]) *Perfum. Record* **10** (1919), 14.

Notes on Scientific Research in the Domain of the Terpenes and Essential oils.

General.

Promotion of the industry of the essential oils in Italy[1]). — According to a draft for a law, dated 17th. November 1918, ground owners who occupy themselves with the cultivation of flowers for the distillation of aromatic essences and oils shall be exempted for 10 years from any ground tax, which is very considerable in Italy. The income due to this occupation shall also be free from income tax. The manufacturers who build or own factories for aromatics and essences shall be exempted for 5 years from income tax or taxes on the buildings (state and local taxes) in so far as these buildings, installations, &c., are to be considered as parts of their works. All machines, installations and building materials, necessary for introducing or carrying on the distillation of aromatics and essences, can be imported free of duty. All these privileges are only meant for Italian subjects, and heavy penalties will be exacted from all who try to be benefitted by them under false pretences.

A lively movement in favour of said industry had already started in Italy some time ago and the necessity of fostering and developing it with all available means was proved. As is well known, the Italian *Citrus* essences belong to the best and most appreciated of their kind and the Cannes or Grasse manufacturers of raw materials for perfumery prepare their finest aromatics mostly from flowers grown on the Italian Riviera.

Essences for perfumery. — The production of essential oils from flowers and aromatic herbs is very inconsiderable in Italy, which is all the more surprising, as the country lends itself so exceedingly well for cultivating all kinds of such raw material. In the neighbourhood of Pancalieri (Piemonte), peppermint has been cultivated on a comparatively large scale for the last ten years or so and the growers are reported to have made considerable profits. In 1917, from 30000 to 32000 kilos of peppermint oil were obtained there. In Piemonte and Liguria (province of Porto Maurizio) about 2000 to 2500 kilos of lavender oil are produced annually, in Sardinia, 400 kilos oil of thyme, 200 kilos myrtle oil, 100 to 800 kilos wormwood oil and 2000 kilos rosemary oil. The Florentine iris is cultivated in Tuscany, wherefrom 60 tons of rhizomes were exported annually, in 1911, 1912 and 1913.

In 1916, the value of non-alcoholic aromatics imported into Italy came up to 1123000 Lire, that of alcoholic ones, to about 1500000 Lire. The exports of these two kinds, however did not even total 1 million Lire. Two thirds of the imports came from France (about 1200000 Lire) and Germany (about 800000 Lire). Artificial aromatic essences came chiefly from Germany; genuine otto of roses, from Bulgaria.

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[1]) *Nachr. f. Handel, Ind. u. Landw.* **1919**, no. 58, page 3. (See foot-note 2 on page 79.)

A great hindrance for the prosperity and the development of the Italian industry of aromatics is the Italian law regarding alcohol, although in decrees of 1905 a partial restitution of the relative taxes in favour of this industry has been provided for.

E. M. Holmes[1]) publishes an article on the cultivation of aromatic plants in Italy, in which he not only discusses the herbs and shrubs which are cultivated already, but also those which either grow wild in sufficient number or might be cultivated there. It is doubtful, whether all the numerous plants mentioned are of real interest, apparently Holmes' treatise is to be taken more as a suggestion for the Italians, how to make proper use of the ressources of their country. In any case, we would recommend reading the article to everybody interested in the Italian flora.

Citrus essences. In 1913, Italy's exports of citrus essences[2]) were: —

Lemon essence . . .	456303 kos.	to the value of	6844545 Lire,
Bergamot essence . .	63093 „	„ „	3911766 „ ,
Orange essence . . .	48103 „	„ „	1010163 „ ,
Mandarin essence . .	913 „	„ „	50215 „ ,
Other citrus essences .	1197 „	„ „	38304 „ .

Of the exports of lemon peel essence, 40 per cent. went to the United States, a further 40 per cent. to England, Germany and France, England being responsible for about half of it. As to bergamot essence, 40 per cent. went to France and 25 per cent. to England. Orange essence was exported to the United States, Denmark and Germany, each country receiving about 1/5 (1/3 ?) of the total. The chief producers are the Citrus Oil Company and the "Soc. Commercio Derivati Agrumari", both in Acireale, and these products served for preparing Eau de Cologne. Before the war, certain quantities of these essences were imported, for instance 16180 kilos in 1906, as compared with only 2800 kilos in 1913. This decided decline of the import of essences and the trifling quantities of fruit bought from foreign essence factories prove the development of the corresponding Italian industry.

As far as figures are available, the exports[3]) of citrus essences were as follows: —

	Bergamot essence kos.	Lemon essence kos.
In 1916	157165	655522
„ 1917	133799	522486
„ January 1918 . .	8163	23144
„ February 1918 . .	10639	66366
„ March 1918 . .	12972	57803.

Prices. The Messina quotations in 1918 were: —

Bergamot essence (basis 38) Lire 22.50 per Italian pound, lemon essence 3.80 per cent. citral 4 Lire, 4 per cent. citral Lire 4.25, sweet orange essence 11 Lire, bitter orange essence 10 Lire, mandarin essence Lire 18.50.

On February 15th, Messina quoted: —

Bergamot essence (basis 38) 19 Lire per Italian pound, lemon essence 3.80 per cent. citral Lire 3.20, 4 per cent. citral Lire 3.50, sweet orange essence 10 Lire, bitter orange essence 8 Lire, mandarin essence 20 Lire.

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[1]) *Perfum. Record* **10** (1919), 33. — [2]) As per reports from Bern, *Nachr. f. Handel, Ind. u. Landw.* **1919**, no. 58, page 4. (The technical terms which are not usual here have been copied literally.) — [3]) See also page 22 of this *Report*.

New factories: Profumeria Inglese, Soc. An. Italiana, Naples, capital 200000 Lire. Società Italiana Profumeria, Milan, Via Castelfidardo 8, capital 160000 Lire.

Ing. Pietro Lanino's work "La Nuova Italia Industriale" contains incorrect figures of the quantities and the value of the Italian exports of citrus essences. The total for 1913 is indicated at about 57000 tons to the value of 21639000 Lire. 50000 tons thereof to the value of 16 million Lire are reported to be lemon essence, so that the price for 1 kilo would be Lire 0.33, whereas according to above February quotation the Italian pound (1/3 kilo) cost from Lire 3.20 to 3.50.

The Industry of the essential oils in Spain[1]) has developed considerably since the outbreak of the European war. The chief districts for herb growing are the provinces of Murcia and Malaga, the favourable climatic conditions of which permit of extending considerably the cultivation and industry. The total production of rosemary, sage, thyme and lavender oils is destined for foreign countries and the export is free of duty. The chief customers are England, France and the United States. In 1916, the United States took essential oils to the value of 211000 Dollars, as compared with 257030 Dollars in the following year. The principal kinds were: thyme oil = $ 157571, rosemary oil = $ 59788, lavender oil = $ 23407, origanum oil = $ 7773, spike oil = $ 4847, other essential oils = $ 3684.

According to an article in the Pioneer Mail of April 17th[2]), it was stated in the last session of the United Provinces Legislative Council (British India) that the provincial government had accepted a plan recommended by the Board of Industries, according to which trials should be made of cultivating flowers containing aromatic substances. The costs are estimated at 5500 Rupees yearly. These trials will extend over a period of three years, to begin with.

In an official Dutch paper[3]) there is an article on essential oils, according to which it is to be presumed that there will be a considerable increase in the demand for essential oils, as soon as soaps and perfumes can be manufactured again on a large scale. For this reason attention is called to the various essential oils produced in the Dutch East Indies, which are: —

Cajuput oil[4]). The *Kajoepoetih* tree occurs in the whole Malay archipelago, in the plain as well as in the mountains, especially on the Moluccas. It does not grow wild in Java. The distillation of oil from the leaves was introduced at the time in Boeroe by Europeans and is now still carried out by natives. There are about 500 small "*ketels*"[5]) working, most of which are the property of Chinese traders. A *ketel* consists of a little wooden building, in which the primitive distillation apparatus is put up[6]). The owners cede the use of this installation against a monthly rent of 10 to 15 guilders; the tenants must bind themselves to sell the oil to the owners of the *ketel*. Under normal conditions, the price was about 80 Dutch cents for a bottle holding 1 1/2 litre. The article is exported in boxes of 12 to 25 bottles, which are supposed to hold 540 grams each. Cajuput oil is frequently adulterated with petroleum, light petroleum, &c., by the natives as well as by the Chinese traders. A means for finding out the adulteration is said to be the simple shaking of a half-filled bottle, when the air bubbles are supposed to disappear at for some time in an adulterated

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[1]) *Bol. Of. de Minas y Metalurgia, Bol. Industrial, Chem. Tr. Journ., Revue des Produits Chimiques.* Comp. *Report* October **1918**, 84. — [2]) *Nachr. f. Handel, Ind. u. Landw.* **1919**, no. 115, page 3. — [3]) *Handelsberichten (Den Haag)* **12** (1918), 340. — [4]) Comp. p. 9 of this *Report*. — [5]) The Dutch word *"ketel"* really means kettle, but in this case a small factory. — [6]) Further particulars are to be found in *Teysmannia*, **1914**, page 33.

product. A beautifully green colour being appreciated, a piece of copper is frequently put into the oil.

In Eastern Asia, cajuput oil is looked upon as a universal remedy.

As is well known, the article is generally exported via Makassar. In Boeroe, the export harbour was Kajeli, up to 1914, but now it is Namlea. The *Residentie* Amboina shipped in 1914 about 37000 kilos to Java and 36000 kilos to Celebes and its *Onderhoorigheden*. This district exported 26000 kilos to Java, 13000 to South and East Borneo, 4000 to Menado, 3000 to the West coast of Sumatra and 2000 to Timor. The most important foreign customer is Singapore, whence the oil is sent to British India and Indochina. The United States used to buy indirectly, and are now buying direct, considerable quantities of cajuput oil. It is employed there in a good many patent medicines. Part of the oil reaches Europe via Amsterdam, London and Hamburg.

The official statistics supply the following export figures, in kilos: —

Destination	1913	1914	1915
Holland	6365	9758	12217
Germany	584	1128	5773
United States	526	11874	15931
Singapore	112005	40658	42090
Siam	1246	—	—
Hongkong	2037	1978	2375
Portuguese Timor	1423	—	564
Other countries	142	73	813
Total	124328	65469	79763.

As may be seen, Singapore has partly lost, during the war, its importance as a port of transit, whereas the direct traffic with America has increased considerably.

Cajuput oil is the only oil distilled in the Dutch Indies from wild plants, all the others being distilled from cultivated ones.

It results from an official enquiry made in 1917, that there were then 18 plantations in Java and Madura, and 2 in the so-called *Buitenbezittingen*, which were dedicated exclusively to plants yielding essential oils. The total area was 3000 hectares, 2700 thereof in Java. A good 2800 hectares are planted with citronella grass. The cultivation of essential oil plants is also carried on in conjunction with other plants in 5 Java plantations and plays quite an unimportant part in 7 other plantations, also in Java. Most of the plantations of aromatic plants (13) are in the Preanger district, 7 in Batavia and 4 in Semarang. Outside Java, there is one plantation in Palembang and one in Banka.

Citronella oil. Citronella grass is supplied to the factories in the main by the natives, already cut, when 25 to 30 Dutch cents are paid per picul[1]).

The cultivation of the plant is very simple. It is propagated by dividing the tufts and grows everywhere, if only the soil is fertile. Under favourable conditions, 1 bouw[2]) yields from 5000 to 6000 kilos of grass, and 7 kilos of oil are obtained from 1000 kilos of grass. Most of the factories are the property of Chinese people. After the prices for the oil had gone up (since 1912), more citronella grass has been grown and the natives are also beginning to dedicate themselves to the distillation.

[1]) 1 picul = about 56 kilos. — [2]) 1 bouw = about 7100 sq. m.

The exports were, in kilos: —

Destination	1913	1914	1915	1916	1917
Holland	10242	11227	55713	14278	5565
id. *"voor order"*	10180	44439	—	—	—
Great Britain	—	1500	60394	151719	213631
France *"voor order"*	21137	31446	38049	40653	15654
United States	6637	25787	63560	196065	204807
Japan	—	5091	12377	19416	50437
Germany	23824	17164	—	—	—
Australia	—	—	—	—	5263
Belgium	2710	—	—	—	—
Singapur	500	—	—	4848	13576
Other countries	—	—	3233	1764	6830
Total	75230	136654	233326	428743	515763

These figures clearly show the tremendous increase in the production of Java citronella oil. In 1917, England and the United States received the largest part of the oil, of late the export to Japan has increased and Australia is mentioned as a new customer.

In Batavia, citronella oil is often sold on forward delivery. The factories mostly buy the whole annual output together with an option for the following crop.

Lemongrass oil. This oil has lost its importance for Java, as the importers prefer the Cochinchina and Reunion products. Besides, it was offered from these quarters to such an extent of late that competition was impossible.

Cananga oil. The cananga tree occurs all over India, but Bantam is the only district where it is really cultivated. The trees to be used must be cut down at a height of 5 m., so that they grow more in breadth. They begin to bear flowers when 5 years old, blossom about twice annually and produce about 60 kilos of flowers per year. In order to produce 1 kilo of oil, 350 kilos of flowers are required at least. Small quantities of the oil are exported but do not appear as yet in the statistics.

Champaca oil. Both the trees which come into consideration for the production of champaca oil occur almost everywhere in India. They bloom all the year round. The natives take the oil as a perfume for fatty oil, which is said to be used as hair oil.

As to Vetiver oil, no export figures have as yet been published.

The Singapore as well as the Java variety of Patchouly[1]) are cultivated in Java. The plant also occurs pretty frequently in North Sumatra, but about 80 per cent. of the total export are supplied by the East coast of this island. The plant attains a hight of 2 to 3 feet. The first cut takes place after about 6 months of growth, can be repeated in another 6 months and several times afterwards. After having been dried, the leaves are packed in bales of about 40 lbs. each. Export figures are not given separately in the official statistics, but the value of the leaves exported in 1911 from Pangkalan Brandan was more than 30000 Dutch florins and that of the exports via Tandjong-Pura more than 12000 Dutch florins. In 1914, Tapa Tuan exported patchouly leaves to the value of about 31000 Dutch florins, Pangkalan Brandan for 7800 and other districts for 1500 Dutch florins. Most of the leaves are destined for Penang. In 1916 the value was 6 Dutch florins per picul.

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[1]) See also page 37 of this *Report*.

Pelargonium species are recommended for secondary cultivation in the most elevated rubber plantations.

In a publication by Schmülling[1]), we find some more notes regarding the number of plantations in the Dutch East Indies, dedicated exclusively or in the main to plants yielding essential oils.

In 1917, there were in the Dutch East Indies 32 plantations, in which only essential oil plants were cultivated, 30 thereof were in Java and Madura and 2 in other parts of the colony. The area under cultivation was 3579, 3290 and 289 hectares, respectively.

Besides, there were, in Java and Madura, 1235 hectares planted with aromatic plants, but in mixed cultivations. As far as Java and Madura are concerned, the proportion between pure and mixed cultivations is 2.5 : 1. There are no mixed cultivations in the other parts of the colony, containing essential oil plants.

In a scientific paper[2]), we found an article on a Chinese aromatic plant, which might come into consideration for the perfume industry. It is the orchid *Cymbidium ensifolium*, which is looked upon in China as the queen of flowers. Yang-Tsen-Kia recently described its cultivation. This orchid is so valuable that it is treated with the greatest care. There must be only one plant in each pot and the temperature must be kept between 17 and 20° in day-time, whereas during the night it ought to be from 12 to 14°. Good ventilation is absolutely necessary, and only rain water must be used for watering. The smell is very intense and sweet.

The same author[3]) has published a treatise on several Chinese aromatic plants, which might become of value for perfumery.

In addition to the above described plant, he mentions: —

Kouei Rhoa (Olea fragrans), the scent of which may be best compared with that of jessamine, cultivated all over China. The fresh blossoms serve for perfuming the sitting-rooms; the dried ones, in the manufacture of confectionery and liqueurs.

Nien Rhoa (Nymphœa). The leaves (?) supply a charming, greatly esteemed perfume.

Tchou-Lang-Rhoa (Chloranthus inconspicuus), i. e., the pearl of flowers. The white flowers of this shrub are used for perfuming tea and act an important part in modern Chinese perfumery.

Mei-Rhoa (Prunus) is the only Chinese plant flowering in winter. The fruits have an acid taste and are employed in confectionery.

Tchow-Mei (Actinida chinensis), a climbing plant, supplies edible fruits and scented blossoms.

Ye-si-min is a kind of jessamine and is used for perfuming liqueurs; a variety of it serves for aromatizing tea.

Cha-Rhoa (Camellia Sasangua)[4]) is used in the preparation of hair oil.

Rhoa Tchiao (Xantholylum alatum)[5]) grows in the provinces of Kwang-si, Canton, Sse-tschwan and Shen-si.

The umbelliferæ *Roui-Shian* ressembles fennel and could be exported on a large scale.

P. Badermann[6]), in an article entitled *Sudanesische Parfüms* (Soudanese perfumes), talks about various aromatic plants occurring in the Soudan, which might be used for preparing perfumes and oils. Perfumes act quite a special part in the toilet

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[1]) *In- en uitvoer*, 4 (1919), 338. — [2]) *Journ. Industr. and Engin. Chemistry* 10 (1918), 1022. — [3]) *Parfum. moderne, Perfum. Record* 9 (1918), 272. — [4]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 163. — [5]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 628. — [6]) *Deutsche Parf.-Ztg.* 4 (1918), 182.

treasures of Soudanese women, but some of them are so intense that they would offend European noses.

All the indigenous perfumes are made from plant material, by methods in practice from olden days.

In the running waters and swamps of the whole Soudan, a kind of rush occurs, the bulbous rhizomes of which yield on pressing an oil of strong violet odour[1]).

A gardenia shrub, growing in the whole South of the Soudan, has large white flowers of a very intense smell from which a strongly scented volatile oil is pressed, which is well fitted for perfumery.

Oil of date-palm is a favourite perfume. It is obtained from the flower-sheaths by pressing as a volatile oil.

The flowers of a Lawsonia shrub supply a volatile oil smelling of lily of the valley and said to be well fitted for perfumery.

Badermann mentions some more plants, supposed to contain essential oils appropriate for perfumery, but does not give any details regarding their botanical origin.

In an English periodical, we find a description and illustrations of two apparatus, patented by the firm of Lautier Fils, which promise to become of importance for the *enfleurage*. The exhausted jessamine flowers are removed within two seconds from the *châssis* with the aid of the larger machine. However, as then tiny particles of the flowers still remain on the fat, a smaller apparatus has been constructed, which by pneumatic force removes them.

Owing to this new method, the fingers never touch the fat and the advantages are considerable saving of time and labour, as well as a reduced loss of fat[2]).

We have reported several times already[3]) on the use of essential oils in the treatment of ores. For this purpose, the "fir oil" obtained in the United States and on which the Board of Trade Journal of 18th July 1918 writes[4]), comes also into consideration. It is true, however, that one cannot gather clearly from this communication what oil is meant.

According to the Weekly Bulletin of the Canadian Department of Commerce the "floating process" for the treatment of ores has made it possible to increase the production considerably. It is stated that 20 per cent. more was obtained in some cases, than with the former methods. Until a short time ago, the process depended on an oil available only in comparatively small quantities. It is known as pine oil and is obtained by distillation of turpentine in those southern regions of the United States, where the "hard" pine grows. The laboratories of the Canadian Forest Department have now discovered a substitute in the hardwood creosote oil, a by-product of the distillation of wood. After trials extending over several months, a pine oil was prepared from the Canadian "red" pine and, in addition, a much cheaper substitute. Both oils were tried by the Mines Branch in Ottawa, in order to ascertain which of the two would be the best fitted for the elaboration of the various Canadian ores. In consequence of the discovery, the mine owners have diverted their attention from the expensive "fir oil" of the United States, and the Canadian substitute, which had been so far a useless by-product of the wood distilling industry, is preferred. The production being now 1200 gallons daily, it is to be presumed that it will not only

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[1]) In connection with this, we would mention that according to Holmes the roots of *Cyperus longus* and *C. rotundus* are used in England in the preparation of lavender water (*Perfum. Record* **10** [1919], 35). — [2]) *Perfum. Record* **9** (1918), 326. — [3]) Comp. *Report* October **1917**, 5. — [4]) *Nachr. f. Hand., Ind. u. Landw.* **1918**, No. 122, p. 5.

be large enough to cover the requirements of the Canadian mining industry, but that there will be some excess available for export.

G. V. Pigoulevsky[1]) determined the constants of a range of Russian essential oils, as follows: —

Sweet basil oil	$d_{4^\circ}^{20,5^\circ}$ 0.9023;	$[\alpha]_D$ — 15.00°
Laurel oil	$d_{4^\circ}^{21^\circ}$ 0.9161;	$[\alpha]_D$ — 22.79°
Rue oil	$d_{4^\circ}^{22^\circ}$ 0.8402;	$[\alpha]_D$ — 0.48°
Rosemary oil	$d_{4^\circ}^{22^\circ}$ 0.8878;	$[\alpha]_D$ — 0.08°
Oil of *Salvia grandiflora*	$d_{4^\circ}^{21,5^\circ}$ 0.8808;	$[\alpha]_D$ — 16.20°
Hyssop oil	$d_{4^\circ}^{22^\circ}$ 0.9349;	$[\alpha]_D$ — 22.59°

The author did not find any new constituents in them.
It is not to be seen from the discussion, in what part of Russia the oils were distilled.

Analytical Notes.

We wish to direct the attention of our reader to an adulterant which recently has found wide-spread employment and has turned out a true curse in the essential oil trade. We mean the dimethyl ester of phthalic acid, *dimethyl phthalate*, which originally was a mere perfume base, but nowadays is used for adulterations to an extent wholly unexpected. It is added indiscriminately to every oil, regardless of the necessity of "improving" or not the ester content, and the adulterators add it in amounts as are quite astounding. A sad proof how the war and its consequences have upset commercial ethics.

Generally, it is easy to detect the presence of this ester, especially when it is a question of stronger adulteration. Rise in the specific gravity and, above all, in the ester value are the strongest symptoms for its presence.

We have discussed, in the present *Report*, the following oils and preparations adulterated with dimethyl phthalate: —

Anethole	p. 63	Cinnamon Oil, Ceylon	p. 18
Bergamot Oil	p. 26	Ionone	p. 68
Caraway Oil	p. 15	Lavender Oil	p. 34
Cassia Oil	p. 15	Peppermint Oil	p. 39

Colour reactions are only of minor importance when testing essential oils, and justly so, since on the whole they are of no use whatever for judging the purity of these products. Utz[2]) has compiled those reactions which may in some cases be of use, taking especially regard of recent publications. Since we have occasionally referred to these, we content ourselves with mentioning the publication.

The estimation of essential oil in non-alcoholic flavouring extracts. — There has been appearing for some years on the American market a variety of so-called non-alcoholic flavouring extracts which consist essentially of an emulsion of the respective essential oils in some gum mucilage. Glycerol is often present. In order to determine the amount of essential oil present, especially in lemon, orange, almond, anise, and

[1]) *Journ. russ. phys. chem. Soc.* **48** (1916), 1047; *Bull. Soc. chim.* IV. **23** (1918), 341. — [2]) *Deutsche Parf.-Ztg.* **5** (1919), 100.

nutmeg extracts, F. M. Boyles[1]) proceeds as follows: 10 cc. of the emulsion are measured into a graduated cylinder and transferred as much as possible into a 50 cc. flask, the cylinder rinsed with 10 cc. portions of 95 per cent. alcohol, and with the aid of a glass rod all of the emulsion and precipitated gum transferred into the flask, filled up to the mark, the contents shaken thoroughly, then let to stand for 1/2 hour. The liquid is then filtered through a folded filter and the oil determined in a 20 cc. portion of the filtrate by the official American method. Steam-distillation gives good results with lemon, orange, and peppermint extracts provided that blank distillations are carried out beforehand with extracts of known oil content so as to ascertain the percentage of oil lost in distillation. Generally, 90 to 95 per cent. of the oil present is recovered.

For cassia, cinnamon, and clove extracts, the following modification was successfully made use of: 10 cc. of the sample are diluted with 95 per cent. alcohol to 50 cc. and then filtered. 10 cc. of the filtrate are placed in a separatory funnel containing 50 cc. water, then 1 cc. HCl (1:1) is added and the liquid shaken out four times with 25 cc. portions of ether. The combined ether extracts are washed with water, dried shortly with calcium chloride, filtered through cotton-wool into a tared beaker, the ether evaporated on a boiling water bath, the residue placed for 3 minutes in a desiccator and then weighed.

For the purpose of *identification of the allyl group* in constituents of essential oils S. Furukawa[2]) recommends Kobert's reaction with phloroglucinol and hydrochloric acid. The red coloration produced by this reagent with certain aromatic compounds is not, as claimed by Kobert, a trustworthy test for the presence of the allyl group. Eugenol and safrole, for instance, give the characteristic coloration only after at least six months' standing at ordinary temperature. On fractional distillation of such oils under reduced pressure, the first fraction does not give the reaction until after a long keeping. Moreover, citronellol and geraniol give a red-brown coloration with that reagent, whilst others, such as citronellal and citronellic acid, do not give any coloration.

We reproduce this abstract without any comment and refrain from any criticism as to the value of this information until after we have studied the original work.

In order to *estimate hydrocarbons* in mixtures, J. Tausz[3]) treats the mixture with acetic anhydride at low temperatures, generally at $-15°$, in special cases at $-80°$. At these low temperatures, the anhydride dissolves out of the mixture the compounds richest in carbon. The aromatic hydrocarbons are dissolved best, next the unsaturated hydrocarbons. The paraffins dissolve most difficultly, in the same way as with sulphur dioxide which, according to Edeleanu, extracts from mixtures principally the unsaturated hydrocarbons. Both methods, the acetic anhydride as well as the sulphur dioxide method, fail, however, in cases where the amount of unsaturated hydrocarbons is too great, since then the hydrocarbons dissolve completely in the solvent.

Inasmuch as the acetic anhydride method might lend itself to the examination of essential oils or terpene hydrocarbons, we gave a short abstract thereof.

When *testing pure geraniol* according to the phthalic anhydride method devised by us[4]) for testing citronella oil for its geraniol content, A. W. K. de Jong[5]) observed values

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[1]) *Journ. ind. eng. Chemistry* **10** (1918), 537; *Journ. Soc. chem. Industry* **37** (1918), A. 530. — [2]) *Journ. chem. Ind.*, Tokio **21** (1918), 513; *Journ. Soc. chem. Industry* **37** (1918), A. 716. — [3]) *Chem. Ztg.* **43** (1919), 252. — [4]) *Report* October **1899**, 24; October **1912**, 43. — [5]) *Koninkl. Akad. d. Wetensch., Amsterdam, Wis- en Natuurkund. Afd.*, **27** (1918), 283. Meeting of Sept. 27, 1918.

corresponding to 89 to 92 per cent. only of the theoretical value, whereas with mixtures of geraniol and citronellal, the method gave very nearly the theoretical value, as was established by ourselves. de Jong is of opinion that in presence of geraniol a part of the citronellal also suffers esterification in the same proportion with the geraniol present.

On the estimation of aldehydes and ketones. — Many methods have been worked out for this purpose and have been discussed for the major part in our *Reports*. L. Lautenschläger[1]) now describes a new method for titrating aromatic aldehydes with hydrazine and for ketones and aliphatic aldehydes with acid hydrazides.

The author has found that the aromatic aldehydes react quantitatively when shaking with the molecular amount of aqueous hydrazine solution. The estimation is carried out as follows: — About 1 g. of the aldehyde under examination is mixed with a certain amount of hydrazine sulphate solution in excess, the strength of which is previously ascertained by titration against iodine. The mixture is then let to stand for a couple of hours, when the following reaction takes place: —

$$2\,R\cdot CHO + N_2H_4\cdot H_2SO_4 = R\cdot CH:N_2:CH\cdot R + 2\,H_2O + H_2SO_4.$$

The solution is freed from the precipitate formed by filtration and the filtrate filled up to a certain volume. In a corresponding part of this solution the amount of the hydrazine not consumed in the reaction is estimated iodometrically by adding a certain amount of iodine solution in excess, then making the liquid alkaline by addition of caustic soda, then acidifying the solution after the evolution of nitrogen has passed off, and titrating the excess of iodine with sodium hyposulphite. The aldehyde present is calculated from the amount of hydrazine sulphate solution taken in reaction, the iodine solution and the hyposulphite solution used for titrating back.

For transforming one molecule of hydrazine into the aldazine, two molecules of aldehyde are required, as is evident from the equation above. Furthermore, 4 atoms iodine correspond to 1 molecule of hydrazine: —

$$NH_2\cdot NH_2 + 2\,I_2 = N_2 + 4\,HI,$$

so that 2 molecules aldehyde are equivalent to 4 atoms iodine.

This method is not applicable with ketones and aliphatic aldehydes, since they react only incompletely, and often not at all, with hydrazine. In such cases the use of acid hydrazides, *e. g.* benzhydrazide, proved to be successful. These hydrazides may equally be titrated iodometrically and react quantitatively with a large number of aldehydes and ketones in accord with the following equation: —

$$C_6H_5CO\cdot NH\cdot NH_2 + OCRR_1 = C_6H_5CO\cdot NH\cdot N:CRR_1 + H_2O.$$

The condensation-products formed are insoluble in water. With the lower aliphatic ketones and aldehydes the reaction remains incomplete but is quantitative with the higher aliphatic aldehydes as well as with numerous carbonyl compounds of the terpene series. The titration is carried out in the same manner as described above with hydrazine sulphate, the interaction, however, between the acid hydrazide and the carbonyl derivatives mentioned proceeds in the most cases far slower than the condensation of hydrazine. The aqueous solution of the hydrazide (the amount of which having been previously estimated iodometrically) is therefore shaken for some time with a weighed amount of the substance under examination, using here again an excess of the hydrazide. The interaction is complete only after 12 to 24 hours, although a precipitate is generally formed immediately after mixing both substances. After that time the precipitate is

[1]) *Arch. der Pharm.* **256** (1918), 81.

filtered off and the hydrazide not having entered the reaction estimated in the filtrate. For accelerating the interaction the substance may be heated with the hydrazide, in alcoholic solution, for some hours on a water-bath under a reflux condenser. Then the alcohol is evaporated and the residue dissolved in water; the acid hydrazide passes quantitatively into the solution, the condensation-product remains back and is filtered off. In the filtrate the hydrazide is estimated by titration against iodine.

How the estimation is carried out by means of hydrazine sulphate solution appears from Lautenschläger's description of his method for determining the vanillin present in vanilla beans: —

3.5 g. vanilla beans are extracted for one hour with 5 cc. boiling diluted alcohol on a water-bath under a reflux condenser. After filtration the alcohol is evaporated and the residue treated with 50 cc. normal hydrazine sulphate solution. After several hours' standing the liquid is filtered and the filtrate brought to 250 cc. 25 cc. of this solution are mixed with 50 cc. decinormal iodine solution, alkalified by means of caustic soda, after short standing acidified with dilute sulphuric acid and the excess of iodine titrated back with sodium hyposulphite solution. For this purpose, 8.1 cc. decinormal hyposulphite solution were required. From these figures, a percentage of 1.7 of vanillin in the vanilla was calculated[1]).

Similarly, he found in Ceylon cinnamon oil 75.9 per cent., in cassia oil 70 per cent.[2]), and in Ceylon cinnamon bark 0.72 per cent. of cinnamic aldehyde.

How the method is carried out when acid hydrazide is employed appears from the following determination of the ketone in carvone: —

1 g. of the substance was heated with 50 cc. alcoholic normal hydrazide solution for five hours on a water-bath beneath a reflux condenser. The alcohol being evaporated, the mixture was treated with water, the precipitate formed filtered off, and the filtrate filled up to 250 cc. with distilled water. 25 cc. of this solution were mixed with 50 cc. decinormal iodine solution and some caustic soda solution, and consumed, after acidification with dilute sulphuric acid, 13.3 cc. decinormal sodium hyposulphite solution. From this value, a carvone content of 99.75 per cent. was calculated.

In the same manner Lautenschläger found in lemon oil 4.7 per cent. aldehydes (citral and citronellal) and in *Spiritus camphoratus, Ph. G.* V, 9.9 per cent. camphor.

The author further determined the percentage values of a number of compounds according to the methods described above and compiled them in tabular form, so as to prove the reliability of the methods. The table, in fact, gives model figures which are in nearly full accord with the theoretical values. The aldehyde content, *e. g.*, was found for benzaldehyde 99.1 per cent., cinnamic aldehyde 100.0 per cent., vanillin 100.7 per cent.

We submitted Lautenschläger's hydrazine sulphate method for examining aldehydes to a test in our laboratory and experienced a sad disappointment, the more so, as the values found were far from being even approximately correct.

We followed the directions (not fully clear) of the author and treated a corresponding amount of the substance under examination with 50 cc. decinormal hydrazine sulphate solution. After occasional shaking the mixture was put aside for several hours and

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[1]) Somewhereabouts there must be a printer's error, for on calculating the figures given by the author the value 17, and not 1.7, results. We were unable to trace the mistake; the correct figure 1.7 is arrived at when it is assumed that 35 g., and not 3.5 g., of vanilla are taken for examination; this amount, however, being rather improbable. Unfortunately, this is not the only misleading erratum in Lautenschläger's paper. — [2]) Cassia oil contains at least 75, mostly even more than 80 per cent. cinnamic aldehyde; supposed that the above figure is correct Lautenschläger has dealt with a quite inferior oil which in all probability was highly adulterated.

even longer. When the action was complete the liquid was filtered and a corresponding part of the filtrate used for titration with decinormal iodine solution.

When 0.1 to 0.2 g. of benzaldehyde were shaken with 50 cc. decinormal hydrazine sulphate solution the interaction manifested itself soon by the formation of a precipitate and by ensuing separation of the aldazine. After letting the mixture stand for 5, 24 and 48 hours there were hardly any differences to be found on subsequent titration. The average value found for the benzaldehyde under examination was 95.5 per cent., the benzoic acid content amounting to 1.6 per cent.

The valuation of cinnamic aldehyde was carried out in the same manner, the interaction passed off somewhat slower. The cinnamic aldehyde in question, which according to the bisulphite process contained 100 per cent. aldehyde, gave on repeated examination by aid of the hydrazine sulphate process values varying between 90 and 93 per cent.

On shaking vanillin with decinormal hydrazine sulphate solution the mixture acquires instantaneously a yellow coloration, the precipitate being formed only after 15 to 20 minutes' interaction. The reaction proceeds only very slowly and appears to be completed, often only after 24 hours' standing, as soon as the turbid liquid has turned fully clear, although it remains more or less yellow. Since with vanillin the analytical values found differed widely, a great number of determinations were carried out with this aldehyde, partly with vanillin as such, partly with its aqueous solution. It was found in these experiments that the aldehyde content found was the lower the smaller the amount of aldehyde was which was treated with 50 cc. decinormal hydrazine sulphate solution. Whereas on examination of

about 0.3 g. vanillin an average of about 90 p. c. aldehyde resulted,
there was found with „ 0.2 „ „ „ „ „ „ 87 „ „ „
„ „ 0.1 „ „ „ „ „ „ 80 „ „ „
„ „ 0.05 „ „ „ „ „ „ 48 „ „ „
„ „ 0.025 „ „ „ „ „ „ 6 „ „ „

On comparing the amounts of vanillin used and found it appears that the difference in both of these figures with each experiment is fairly constant: —

Amount analyzed	0.305 g.	0.206 g.	0.104 g.	0.054 g.	0.0250 g.
ditto found .	0.277 „	0.180 „	0.083 „	0.026 „	0.0015 „
Difference:	0.028 g.	0.026 g.	0.021 g.	0.028 g.	0.0235 g.

The mean difference is, therefore, 0.025 g., *i. e.*, in each test this amount of vanillin is not found, it being uncertain whether or not this amount is combined with hydrazine. In any case, these experiments proved that vanillin does not react quantitatively with hydrazine sulphate under the conditions suggested.

The vanillin tested showed the m.p. 82 to 83° and on examination according to Hanuš'[1]) method with *p*-bromophenylhydrazine proved to be, on the average, 100 per cent.

It deemed not necessary on account of the results mentioned above to subject Lautenschläger's hydrazide method to a trial test, but at all events we point out that with citronellal the author found 101.3 per cent., whereas, according to our observations[2]), a 100 per cent. citronellal is difficult or even impossible to prepare.

R. S. Hiltner[3]) had worked out *a colorimetric method for determining the citral content* of lemon extracts and in lemon oils basing on the yellow coloration imparted to a dilute alcoholic solution of *m*-phenylene diamine hydrochloride, at room temperature,

[1]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **3** (1900), 657. — [2]) *Report* October **1912**, 41. — [3]) *Journ. ind. eng. Chemistry* **1** (1909), 798. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 40.

on addition of citral, the coloration becoming deeper the higher the citral content is. In this determination it not infrequently occurs that lemon and orange oils and extracts produce blue or green colours instead of yellow, thus restricting the applicability of the method. C. E. Parker and R. S. Hiltner[1]) are of opinion that this abnormal reaction is due to the presence of oxygenated bodies, such as peroxides, in the oils. In addition, the preliminary treatment of the bodies under examination is responsible for the behaviour towards the reagent. By way of experiment it was found that commercial *d*-limonene[2]) and commercial turpentine oils give a decided blue coloration with phenylene diamine solution, but not citral. An orange oil which failed to give the blue coloration was exposed to the air by standing overnight in a shallow receptacle, and also by bubbling air through it for one-half to four hours, after which it gave a blue colour with the reagent in a short time.

Stannous chloride was found to prevent the formation of the blue colour, but the turbidity resulting from the formation of basic tin compounds was a complication leading to its rejection. Sulphurous acid and *m*-phenylene diamine sulphite were tried, but with them citral produced no yellow colour. The most convenient way was to add a proper amount of oxalic acid to the original Hiltner reagent, and this procedure was tried upon a number of lemon and orange oils and extracts with entirely satisfactory results, the only colour aberration so far observed being a slightly brownish tinge developed in some cases.

The improved Hiltner method is carried out as follows: —

The citral standard solution contains in 1 cc. 0.001 g. citral; the alcohol must be practically colourless and 94 to 95 per cent. strength and need not be aldehyde-free.

The *m*-phenylene diamine-oxalic acid solution is prepared by dissolving 1 g. *m*-phenylene diamine hydrochloride and 1 g. crystallized oxalic acid each in about 45 cc. of 80 per cent. alcohol. Both are mixed in a stoppered 100 cc. graduated flask or cylinder and made up to the mark with 80 per cent. alcohol. 2 or 3 g. of Fuller's earth are added and shaken well, then the liquid is allowed to settle nearly clear and decanted upon a double filter.

For carrying out the assay, weigh into a 50 cc. graduated flask about 0.5 g. of a normal lemon oil, or about 4 g. of orange oil, or 10 g. of lemon extract, or 50 g. of orange extract, and make up to the mark with 94 per cent. alcohol. Pipette an exactly measured amount (say 5 cc. of this "first dilution") into a 50 cc. graduated flask. Pipette also 4 cc. of the standard citral solution (0.1 per cent.) into a 100 cc. graduated flask. As nearly as possible at the same time add to the 50 cc. flask, 10 cc., and to the 100 cc. flask, 20 cc. of the phenylene diamine solution, fill up to the marks with 94 per cent. alcohol, stopper and mix well. Both solutions are transferred to a colorimeter and compared with each other; from the preliminary result the approximate citral content of the unknown solution and a "second dilution" of the latter is calculated which is again compared with the standard.

Determination of methoxyl by means of pyridine. — The estimation of the methyl value according to Zeisel[3]) is easy to carry out, but to some extent a round-about and time-taking method. It may, however, be shortened, as A. Kirpal and Th. Bühn[4]) have communicated. The former had observed accidentally that pyridine methyl iodide, in absence

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[1]) *Journ. ind. eng. Chemistry* **10** (1918), 608. — [2]) Evidently, the limonene sample examined was highly resinified and consequently oxygenated or contained peroxides, since the authors describe their sample of "limonene, pure, Schimmel & Co." as being quite yellow and syrupy! — [3]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 598. — [4]) *Berl. Berichte* **47** (1914), 1084.

of pyridine and its salts, may be titrated smoothly with silver solution, with sodium chromate as indicator; since, furthermore, it had been found that pyridine is able to absorb quantitatively methyl iodide from strongly diluted gas mixtures, with formation of the iodomethylate, a means was given hereby to abandon the silver solution when estimating the methoxyl content of sulphuretted substances.

On these grounds, J. Th. Hewitt and W. J. Jones[1]) suggested a modification of the usual methoxyl estimation process.

The hydriodic acid was prepared by saturating an aqueous suspension of iodine with hydrogen sulphide, distilling the resulting solution, and collecting the fraction boiling between 123 and 127° (d 1.7). The pyridine need not be entirely freed from picoline; however, it is advisable to remove substances of high boiling point.

The apparatus consists of the usual carbon dioxide generator, the decomposition flask heated in a glycerol bath to 130°, and rectifying column (four-pear or other suitable form). The carbon dioxide carrying the methyl iodide vapour is passed through two test-tubes in series, each containing 10 cc. of pyridine. Removal of the excess of pyridine before carrying out the titration is, according to the authors, unnecessary.

For the estimation, a suitable weight of the substance is taken, 20 cc. of hydriodic acid (d 1.7) are added, and the heating maintained for one hour. The contents of the test-tubes are completely washed into a graduated flask, when they are diluted with water. The iodine ion is titrated, after acidification with nitric acid, by adding a known amount of standard silver nitrate solution and titrating back the excess of silver by thiocyanate according to Volhard's method.

In the course of the experiment, a yellow coloration develops in the pyridine. This vanishes on dilution of the pyridine at the and of the experiment. It is not due to free iodine. Should, however, the colour persist on dilution with water, it is then advisable to discharge it with thiosulphate solution.

The analyses demonstrated, *inter alia:*—

	Percentage of methoxyl group	
	found	calculated
Methyl alcohol .	95.2 to 96.3 per cent.	96.9 per cent.
Methyl salicylate	19.7 per cent.	20.4 per cent.

Unsatisfactory results were obtained with methyl benzoate.

In our opinion, it remains to be proved whether the method is suitable for estimating essential oils.

Some years ago, C. A. Hill and T. T. Cocking[2]) described a quantitative method for *estimating cinnamic acid in storax* which, briefly spoken, based on the fact that the saponified balsam was dissolved in water, extracted with ether, and acidulated; by renewed extraction with ether the cinnamic acid is shaken out and estimated. This method (now official in the British Pharmacopœia, 1914) has been tried by Cocking and Kettle[3]) for the estimation of the aromatic acids in *balsam of tolu*, but was abandoned, as repeated extractions by boiling with water caused the resinous matter to become so stiff that it was impossible to extract the acids completely. It was found, however, that boiling out of the aromatic acids with magnesium oxide and water, in the presence of a small quantity of xylene to soften the resin, was the most satisfactory way of dealing with the balsam. The magnesium salts of the aromatic acids are readily soluble in cold water, those of the resin acids being insoluble.

[1]) *Journ. chem. Soc.* **115** (1919), 193. — [2]) *Chemist and Druggist* **80** (1912), 412; *Report* October **1912**, 126. — [3]) *Americ. Journ. Pharm.* **90** (1918), 719.

The mode of procedure is as follows: —

1. *Estimation of the Free Balsamic Acids.* — 5 gr. of balsam of tolu are dissolved in 25 cc. of hot alcohol in a 250 cc. CO_2 flask, 5 g. of light magnesium oxide and 20 cc. of xylene are added, and the flask shaken round until the contents are well mixed. One hundred cc. of water are now added, the flask connected to a reflux condenser and boiled for one hour. After cooling, the whole is poured on a Buchner filter, and the aqueous portion of the filtrate separated from the xylene layer, which is returned to the flask together with the filter paper and the adhering magnesia-balsam magma. A second 100 cc. of water is added, and the flask again boiled for an hour when the aqueous portion of the filtrate is separated off as before and the extraction carried out a third time. The bulked aqueous liquids are washed once with 20 cc. of ether, then rendered acid with hydrochloric acid, and the precipitated acids extracted by shaking out with ether. The greater part of the ether is distilled off, and the residual aromatic acids dried *in vacuo* over sulphuric acid and weighed.

2. *Estimation of the Total Balsamic Acids.* — 2.5 g. of balsam of tolu are saponified by boiling with excess of alcoholic potash; most of the alcohol is then evaporated off, the residue dissolved in 100 cc. of hot water, and sufficient hydrochloric acid added to render the whole slightly acid. 5 g. of light magnesium oxide and 20 cc. of xylene are next added and the whole boiled up under a reflux condenser for one hour. The aqueous liquid is separated, the extraction repeated twice, and the bulked aqueous liquids treated as in the case of the free balsamic acids.

The proportion of cinnamic acid is determined by the gain in weight on bromination[1]).

The aromatic acids obtained from balsam of tolu are not quite so pure as those from benzoin and storax. The brominated acids from the two latter are white and pleasant-smelling, while those from tolu are slightly brown in colour, and contain a substance which is extremely pungent and lachrymatory.

Balsam of tolu, as a rule, contains very little that is not soluble in alcohol, but occasionally samples are met with containing woody matter. Three such samples contained 1.6, 8.9, and 9.0 per cent. of insoluble matter.

Moisture, generally present, was estimated by spreading in a thin layer on a sheet of glass and drying *in vacuo* over sulphuric acid. Amounts varying from 2.0 to 8.6 per cent. were found, and the dried balsam was usually quite brittle.

The determination of the acid value of the balsam is somewhat difficult owing to the dark colour, and to the precipitate which is formed on running in the alcoholic potash. The authors, therefore, dissolve 5 g. of the balsam in about 50 cc. of boiling alcohol, add a large quantity of phenolphthalein solution — 3 or 4 cc. — titrate the hot solution with normal alcoholic potash until the colour becomes dark brown (but not red), then attach to a reflux condenser, boil up for a few minutes in order to break up the precipitate, and finish the titration.

Cocking and Kettle observed the following values in connection with numerous samples: —

92.2 to 132.4 for acid value,
59.3 to 90.9 for ester value,
154.8 to 206.7 for saponification value,
32.68 to 47.50 per cent. of total balsamic acids.

As to the *sensitiveness of the cineole-iodole test,* see p. 67 of this *Report.*

Concerning the *estimation of benzaldehyde, vide* p. 66 of this *Report.*

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[1]) *Year Book of Pharmacy,* **1914**, 355.

Re the *identification* and *estimation of coumarin in artificial vanilla extracts,* comp. p. 67 of this *Report.*

As to the *identification of* p-*cymene,* see p. 56 of this *Report.*

Concerning the *smell as being used as analytical criterion, vide* p. 105 of this *Report.*

On the *estimation of menthol in solution with phenol and eugenol,* comp. p. 69 of this *Report.*

Re the *estimation of pulegone and of other ketones in American pennyroyal oil,* see p. 37 of this *Report.*

As to some *methods for testing oil of turpentine,* compare p. 51 of this *Report.*

On the use of *thymolsulphophthalein as indicator* in acidimetric work, *vide* p. 75 of this *Report.*

Physical Notes.

Correct determination of boiling points. — Although the boiling point of a body is an important criterion, and although a vast amount of literature has accumulated as to how that constant has to be taken, nevertheless the sources of errors are frequently not taken into due consideration. Theoretically it is agreed upon that reliable results are only obtainable when the liquid, the vapour, and the mercury thread of the thermometer are of the same temperature; in practice, many blunders are committed in this respect.

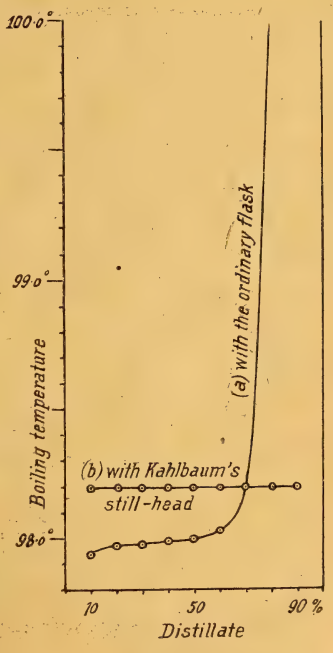

Fig. 1.

Th. Paul and K. Schantz[1]), for instance, demonstrate that the usual boiling-point method for the identification of pure bodies (official in the Ph. Germ.) — boiling flask heated in Babo's air-bath — is faulty to a great extent. In order to bring the liquid to its boiling point the air-bath must be heated comparatively high. This superheating manifests itself principally towards the end of the distillation, when only a little substance is in the flask, and gives rise to an increase of the temperature of both the vapour and the thermometer, as was proved by a series of boiling tests with water and other liquids, where in lieu of a boiling *point,* constantly a boiling *range* of a couple of deg. Cent. was observed. The diagram illustrates which differences come into consideration, curve *(a)* giving the boiling point in an ordinary flask, curve *(b)* with use of a still-head according to Kahlbaum.

An additional error of the Ph. G. method is that a part of the mercury thread of the thermometer projects beyond the flask, which circumstance becomes noticeable especially with higher boiling points and which is eliminated only with difficulty.

[1]) *Arch. der Pharm.* **257** (1919), 87.

Likewise, the Ph. G. does not consider the barometric pressure. The authors have worked out a table from which the b. p. of the drug concerned corresponding to the pressure ruling can be read. For a part of the comparative tests, the boiling points were determined in connection with an atmosphere kept at 700 mm. pressure.

The different parts of the usual apparatus were likewise tested as to their influence on the determination of the boiling point such as the material, size, and filling of the boiling flask, the mode of heating and of illumination (heat radiation!), rapidity of distillation; nothing new, however, was revealed by these small differences.

Finally, the authors report on the influence exerted on the b. p. by the presence of small amounts of foreign substances. The observations recorded fall within the scope of the well-known general laws of vapour pressure of liquid mixtures; they may be briefly referred to in the following review: —

Ethyl ether, pure, + 0.11 to 2.03 per cent. water: depression down to a limit value
Æther pro narcosi + 0.13 „ 2.31 „ „ „ : „ „ „ „ „ „
Ether, *Ph. G. V.* . + 0.13 „ 1.52 „ „ „ : „ „ „ „ „ „
Ethyl ether, pure, + 0.23 „ 1.73 „ „ alcohol: exaltation in proportion to the alcohol added

(pure ethyl ether + 1.15 per cent. alcohol + 1.8 per cent. water has the same boiling point as pure ether)

Chloroform . . . + 0.39 to 2.63 per cent. alcohol: depression
„ . . . + water: „
Ethyl bromide . . + 0.30 to 1.19 „ „ „ : „
„ „ . . + water: „
Benzaldehyde . . + 0.22 to 0.69 „ „ benzoic acid: depression.

We supplement theabove statements insofar that air, either dissolved or introduced, may lead to an oticeable depression of the boiling point.

In the course of their investigation, Paul and Schantz constructed the boiling point apparatus which combines Beckmann's contrivance with Kahlbaum's still-head. Illustration and description are taken from the authors' paper.

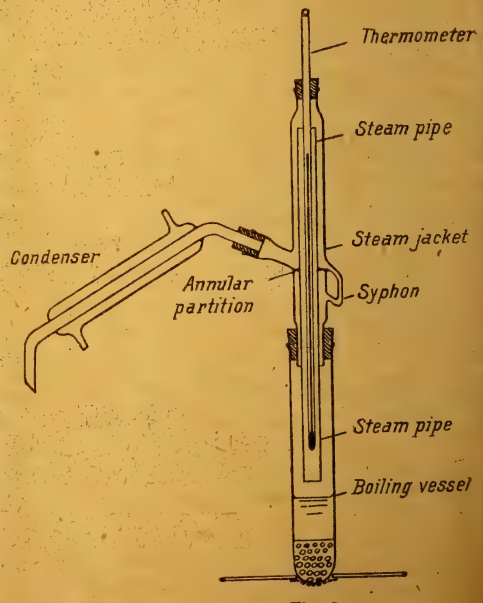

Fig. 2.

A thick-walled test-tube of about 18 cm. height and 20 mm. inside width serves as distilling flask. Tare garnets of 2 to 2.5 mm. diameter are filled in the tube about 3 cm. high, then a sufficient amount of the liquid under examination so that the surface extends about 3.5 cm. above the garnets; about 15 c.c. are required therefor. The still-head is then fixed to the boiling tube by means of a cork, or is ground in. It consists of a vapour tube of about 11 mm. inner width and 23 cm. eight, the upper part of which is fused to, and surrounded by, a steam-jacket of about 20 mm. width and 20 to 22 cm. length. This steam-jacket tapers slightly at its lower part where it fits into the boiling tube. The annular joint, termed "annular partition" in the figure, separates the steam-jacket into an upper and a lower part and is situated about 14 cm. above the

lower end of the steam-tube. The upper end of the steam-jacket tapers likewise and is closed by a cork carrying the thermometer. Directly above the partition, a syphon is connected in order to conduct the condensed liquid back into the boiling tube. The syphon is bent down slightly, before entering the lower part of the steam-jacket, so that a small amount of liquid may accumulate therein and thus block up the connection for ascending vapours. At the opposite side of the steam-jacket the outlet pipe branches off which first is bent upwards and is connected with the efflux condenser by a cork or by grinding-in. The jacket of the condenser measures about 10 cm. The boiling vessel stands in the centre hole of an asbestos plate with a diameter of 2 cm., and closed beneath with brass wire gauze. The asbestos plate must be sufficient in size (diameter about 10 cm.) so as to keep off the radiant heat of the burner from the thermometer. It is advisable, especially with liquids boiling above 100°, to surround the boiling tube with an air-jacket of 5 cm. diameter and 22 cm. height. The thermometer must be inserted sufficiently deep into the steam tube so that the mercury thread is to its whole extent surrounded with living steam. The height of the flame must be regulated so that the liquid just comes to vivid boiling.

We beg to add two remarks in addition to the preceding abstract.

The one of them comprises the suggestion to make use of certain *standard pressures* when quoting boiling points, more especially vacuum boiling points. At present, every author quotes the pressure as recorded directly by his apparatuses, and leaves it to his fellow-chemists how to make use of his statements. Recalculation for the differing purposes of other authors must, therefore, be repeated so often as use is made of the statement concerned. It goes without question that scientific technique would derive a great benefit from the adoption of a certain standard pressure to which the vacuum readings should in future be adjusted.

For ordinary distillations, a normal pressure is given by the "mean" barometric height of 760 mm. mercury column. For vacuum boiling points, C. von Rechenberg (*Theorie der Gewinnung und Trennung der ätherischen Öle*, Leipzig 1910) made use of certain pressures: 10, 20, 50, and 100 mm. mercury. All these quantities are, however, in no connection with the scientific system of measurement. Hence, it seemed advisable to resort to the absolute unit of pressure, termed one "bar" and defined as the pressure of one dyne on one square centimeter. One atmosphere equals 1013200 "bars". Of the multiples of this unit lying in the neighbourhood of the usual vacuum pressures, 10000 "bars" (= 10 "kilobars") corresponds nearly to 7,5 mm., and 20 "kilobars" to 15,0 mm. mercury; both pressures are, therefore, serviceable as standard pressures and may be supplemented by the multiples 100 "kilobars" = 75,0 mm. and 1000 "kilobars" = 750 mm. In this way, the "atmosphere" would come in connection with the absolute system of measurement, a fact to which already Ostwald[1]) has drawn attention.

As was remarked above, this suggestion as to normal pressures alone is not sufficient. If it really shall be a question of saving accessory work, the statements concerning boiling points in the literature must be recalculated, at least as far as they are quoted by the text-books. On the other hand, fellow-scientists should endeavour to recalculate their new readings taken at optional pressures to one of the normal pressures, or still better make use directly of a normal pressure. The contrivances required therefor are universally known; in the simplest form they consist of a throttle cock in connection with a second cock for exact regulation, about in the manner of fig. 3.

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[1]) *Grundriss der allgemeinen Chemie*, Leipzig 1899, p. 54.

The second matter pertains to observations made already in the afore-said book of C. v. Rechenberg concerning the *measuring of the pressure in vacuum distillation.* The author questions, on p. 477, line 8 from below of his book, the correctness of the boiling points in high vacuum in case the pressure is read off behind the receiver. This doubt is fully justified, as has been proved in the meantime by experiments of ourselves which manifested that already below 10 mm., still more below 6 mm., considerable deviations occur, which in some cases amount to a multiple of the pressure indicated. It would lead too far to go into the experimental details; we intend to publish the respective work elsewhere before long. We confine ourselves to resuming the results which show that the incorrectness of the usual method of inserting the

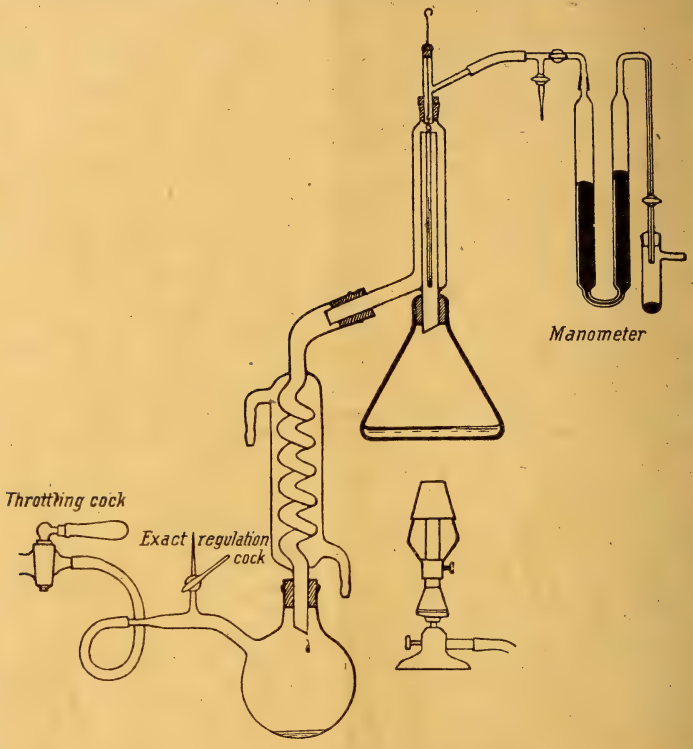

Fig. 3.

vacuummeter into the vacuum pipe rises in proportion to the height of the vacuum, the rapidity of the distillation, and inversely to the diameter of the discharge and condenser tubes, as well as to the leaks in the distillation apparatus. The capillary air-current needed for avoiding the bumping may easily be kept below the measurable, or the noxious, limits.

These facts show how necessary it is to abandon the usual way of connecting the vacuummeter and to attach it to the place where the boiling temperature is read off. Such an arrangement is described on pp. 482 and 483 of v. Rechenberg's book; fig. 3 (above) represents likewise an arrangement answering the requirements of practice.

Relations between boiling temperature and vapour pressure.— Theoretical views as to the vapour tension curves of homologous series of optically active bodies are given

in a paper of H. Schumacher[1]). In homologous series, the ratio of the rotation, with reference to the same wave-length, for normal dispersion, is constant throughout the whole spectrum. The author suspected that for such substances the rule of Ramsay and Young (formally resembling the above law) might also apply to such substances, so that the ratio of the boiling points given in absolute counting and referred to the same pressure, would be, with a series of closely related bodies, independent of the pressure. In order to test his supposition, Schumacher plotted the vapour tension curves of 17 optically active bodies, which actually answered the rule of Ramsay and Young. The bodies studied were: — The menthyl esters of acetic, propionic, *n*-valeric, acetoacetic, methyl, ethyl and *n*-propyl acetoacetic, phenylacetic, phenylethylacetoacetic, phenylacetoacetic, and phenylbenzoylacetic acids, furthermore, the myrtenyl esters of crotonic and of hexahydrobenzoic acids.

The rule of Ramsay and Young applies within the limits of the experimental errors. The tension curves may be calculated, with 1 per cent. deviation, from Rankine's formula: — $\log p = a - b/T$. For particulars of the method and the results, wa refer to the dissertation of the author (Basle, 1917).

Some time ago, Ph. A. Guye[2]) and C. M. Guldberg[3]) found, independantly and nearly simultaneously, that the absolute boiling temperature, at 1 atmosphere pressure, amounts to about two-thirds of the absolute critical temperature, whereas Guye demonstrated furthermore that the absolute boiling point *"in vacuo"* approximates about one-half of the absolute critical temperature. Recently, W. Herz[4]) drew general attention to these papers, and now W. P. Jorissen[5]) deals with the same subject in a paper entitled, *"A relation between boiling points under 1 atmosphere pressure and in vacuo"*.

From the relations found by Guye, the following ratio may be deducted: —

$$\frac{T_{s\,(20\,mm.)}}{T_{s\,(1\,atm.)}} \sim 0.78, \qquad (1)$$

$T_{s\,(20\,mm.)}$ and $T_{s\,(1\,atm.)}$ standing for the absolute boiling points and the sign $\sim$ meaning "approximately equal". Jorissen calculated this ratio from 23 figures published by Guye and found values between 0.71 and 0.84; furthermore, he calculated from data compiled by R. Kempf[6]) the ratio for boiling points under 1 atm. pressure and *"in vacuo"*, amongst these the following of bodies which are of special interest for us: —

Substance	B. p. (1)	mm.	B. p. (2)	mm.	$\frac{T_{s(1)}}{T_{s(2)}}$
1:2-Bromostyrene . . .	108°	20	219 to 221°	1 atm.	0.77
Methyl formiate	95°	10 to 11	219°	1 atm.	0.75
n-Caprylic acid	123.5 to 124.3°	10	236 to 237°	761.7	0.78
Atractylol	162°	15	290 to 292°	760	0.77
Thioborneol	94 to 95°	12.5	224 to 225°	760	0.74
1-Methyl ketone of homoterpenylic acid . . .	205 to 210°	21	330°	1 atm.	0.79
Camphenilane aldehyde .	90°	10	220°	1 atm.	0.74
Phenyl acetic acid . . .	144.2 to 144.8°	12	265.5°	1 atm.	0.78
Cedrol	149 to 155°	8	291 to 294°	760	0.75
Kessyl alcohol	155 to 156°	11	300 to 302°	1 atm.	0.75
Kessyl ketone	162 to 163°	11	305 to 307°	1 atm.	0.75
trans-Pinol glycol . . .	157 to 158°	12	281 to 282°	760	0.78

[1]) *Arch. Sc. phys. et nat.*, Genève (4) **36** (1918), 36; *Chem. Zentralbl.* **1918**, II, 597. — [2]) *Bull. Soc. chim.* III. **4** (1890), 262. — [3]) *Zeitschr. f. physik. Chem.* **5** (1890), 374. — [4]) *Zeitschr. f. anorgan. Chem.* **94** (1916), 1; **95** (1916), 253; **96** (1916), 289. — [5]) *Ibidem* **104** (1918), 157. — [6]) *Tabelle der wichtigsten organischen Verbindungen, geordnet nach den Schmelzpunkten.* Braunschweig 1913.

Now, in 1916 J. J. van Laar[1]) deducted, from van der Waals' vapour pressure formula, a relation which, as he showed later on[2]), equally leads to a formula showing the constancy of the quotients of corresponding temperatures (*vide* formula 1). The value 0.75 was found when certain assumptions were taken as probable.

Jorissen demonstrates furthermore that this constancy of $\frac{T_{s\,(1)}}{T_{s\,(2)}}$ has been deducted already by Clausius[3]) from a formula of J. A. Groshans[4]) and was formulated by him as follows: When the temperatures are counted from — 273°, all the corresponding temperatures are, for any two liquids, in proportion[5]).

Many years later, Groshans[6]), evidently without knowing the relations found by Guldberg and Guye, made use of his formula for comparing the absolute boiling points under 12 mm. and 760 mm. pressure, *e. g.*, for the following substances: —

Substance	B. p. 12 mm.	B. p. 760 mm.	$\frac{T_{s\,(12\ mm.)}}{T_{s\,(760\ mm.)}}$
n-Capronic acid . . .	95.1°	205.8°	0.77
o-Cresol	79.8°	185.5°	0.77
p-Cresol	89.6°	199.0°	0.77
Benzyl alcohol . . .	94.6°	207.0°	0.77
Phenylacetic acid . .	144.5°	265.5°	0.78
Hydrocinnamic acid .	152.2°	280.0°	0.77

Later on, however, Groshans[7]) no longer acknowledged the general applicability of the formula.

Finally, formula (1) is of some importance in publications by U. Dühring[8]) and by Ramsay and Young[9]) resulting in certain simplifications of general vapour pressure laws. At any rate, the formula is only of approximate validity and may have weight with chemically closely related bodies, but shows considerable differences with substances different in constitution.

The polarization phenomena with menthone have been investigated by numerous chemists[10]); they are of special interest, as they are quite unique in the terpene series.

This subject, the rotatory dispersion and inversion of *l*-menthone, has recently been studied by H. Grossmann and K. Brauer[11]). The menthone investigated by them had $d_{4^0}^{20^0}$ 0.8954.

Firstly, the rotatory dispersion of *l*-menthone was determined[12]). The result was: —

Kind of light (l = 2 cm.)	red	yellow	green	l. blue	d'k. blue	violet
a	— 3.92	4.98	6.05	7.15	8.33	— 9.56°
$[\alpha]$	— 24.89	27.81	33.78	39.83	46.52	— 53.38°

in sodium light, with l = 10 cm., a = — 28.46°; $[\alpha]$ = — 28.46°[13]).

The quotients of dispersion were: —

$$\frac{[\alpha]_v}{[\alpha]_r} = 2{,}44 \text{ and } \frac{[\alpha]_{l\,bl}}{[\alpha]_r} = 1{,}82^{14}).$$

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[1]) *Versl. Kon. Akad. v. Wetensch.*, Amsterdam, May 23, 1916, p. 1650; *Chem. Weekbl.* **14** (1917), 808. — [2]) *Ibidem* **14** (1917), 809. — [3]) *Poggendorff's Annalen* **82** (1851), 274. — [4]) *Ibidem* **78** (1849), 112. — [5]) *Ibidem* **82** (1851), 142. — [6]) *Darstellung der physikalischen Eigenschaften der chemischen Verbindungen* $C_pH_qO_r$ *als Funktionen der Atomsumme oder Densitätszahl* $p + q + r$. Berlin 1895. — [7]) *Wiedemann's Annalen* **61** (1897), 142. — [8]) *Neue Grundgesetze zur rationellen Physik und Chemie, 1. Folge,* Leipzig 1878, p. 78; E. and U. Dühring, *Neue Grundgesetze zur rationellen Physik und Chemie, 2. Folge,* 1886, p. 111; U. Dühring, *Wiedemann's Annalen,* **11** (1880), 163; **51** (1894), 223; **52** (1894), 556. — [9]) *Phil. Mag.* (5) **21** (1886), 33. — [10]) Comp. *inter alia, Report* October **1918**, 97. — [11]) *Journ. f. prakt. Chem.* II. **98** (1918), 9. — [12]) All the optical measurements were carried out at 20°. — [13]) Apparently, it is the case of a misprint in the original paper concerning one of these values. — [14]) These values are not correct, but agree for the ratios $\frac{\alpha_v}{\alpha_r}$ and $\frac{\alpha_{l\,bl}}{\alpha_r}$.

Next, the rotatory dispersion of *l*-menthone was determined in the same manner in various organic solvents. It would lead much too far to quote here the values found with each of the solvents, so we must confine ourselves to characterize briefly the influence of some of the solvents, and state merely that with a concentration of 5 g. menthone in 100 cc. the specific angles of rotation lay, with red light, between — 13 and — 25° and with violet light between — 35 and — 60°. The quotients of dispersion with *l*-menthone ranged between 2.16 and 2.80.

Benzene and toluene cause a marked reduction in the rotatory power compared with the rotation of pure *l*-menthone. In toluene, the dispersion quotient is the largest of all observed with this ketone at ordinary temperature, with exception of those cases where inversion takes place. The influence of alcohols on the rotatory power of *l*-menthone seems not to be very great, and in ether, the rotation was even nearer to that of the undiluted ketone than in dilution with alcohols. Benzaldehyde manifested no strong influence on the rotation which, on the whole, was lowered. The values found in acetone solution resemble those observed in ether and approximate the values found with the pure ketone.

Since Beckmann's investigations have shown that some inorganic acids cause inversion of *l*-menthone, the authors studied the influence of numerous acids. However, at ordinary temperature no inversion took place with acetic, propionic, *n*-butyric and *iso*-butyric acids, formic acid being an exception. The acids lower the specific rotation of the ketone, although not so marked as does benzene. The influence of acetic anhydride on the rotatory power of *l*-menthone is even less than with acetic acid; in ethyl acetate and in ethyl acetoacetate solution, the rotation differs hardly from the rotation of the pure ketone.

The halogenated compounds: chloroform, symm. dichloroethylene, trichloroethylene, *o*-dichlorobenzene, and bromobenzene do not act in the equal sense on the rotation of menthone. Di- and trichloroethylene are of hardly any greater influence than for instance ethyl alcohol; the chloro derivatives of benzene cause a depression in the rotation, whereas chloroform raises the specific rotation by nearly 13 per cent. Thus, chloroform shows an influence opposite to that of all other solvents investigated which lower the rotation more or less.

The solutions of menthone in aniline and dimethylaniline were difficult to investigate since they soon turned brown. Of nitrogenous bodies, the following were examined: aniline, dimethylaniline, nitrobenzene, benzyl cyanide, and pyridine. Nearly all of them give rise to a marked reduction of the rotatory power, with the sole exception of nitrobenzene. Carbon disulphide is of only little influence on the specific rotation of menthone.

The numerous publications on the so-called inversion of *l*-menthone are dealt with critically by the authors. They are of opinion that hitherto an exact proof was missing as to the fact that the inversion-products of *l*-menthone with different rotation are not optical antipodes. Difficult as the proof by chemical means may be, it is a very easy one by physical, *i. e.* optical means, the measuring of the rotatory dispersion of *l*- and of the so-called *d*-menthone giving the most certain evidence that the two optical isomerides are completely different, whereas the agreement, in yellow light, is a mere chance.

The authors then prepared, with special caution, a dextrorotatory menthone (II) after Beckmann's directions; a preparation (I) obtained under the conditions originally devised by Beckmann showed a lower rotation. In addition they examined a third menthone (III) handed over to them by other investigators. The values observed with these three ketones show evidently that none of these dextrorotatory menthones is the

antipode of *l*-menthone. The clearest evidence in this respect is furnished by the dispersion ratios, which with the menthones II and III (resembling the true antipode of *l*-menthone strongly on account of their rotation in yellow light) amounts to 3.93 to 3.47, whereas with *l*-menthone the ratio was only 2.43.

Furthermore, the authors thought it possible that the different menthones might also show differences in their refractory dispersion and they investigated, consequently, the refractory power also in other spectral colours. The measurements of the refraction proved, however, that no considerable differences occur between *l*-menthone and *d-iso*-menthone, a fact which would seem to indicate that the so-called inversion involves no serious chemical changes, but merely steric alterations.

The inversion of menthone is effected by certain reagents, principally acids. It appeared to the authors to be of special interest to investigate the chemical processes occurring when menthone is dissolved in pure acids which cause inversion.

The *l*-menthone was first dissolved in a series of organic acids. At ordinary temperature, however, no formation of a dextrorotatory isomer was observed with acetic, propionic, butyric, and *iso*butyric acids. But after boiling of these solutions, the menthone proved to be dextrorotatory.

The high dispersion ratio shows that in all solutions and also in the menthones separated off there are formed, for the greater part, dextrorotatory isomerides. The rotatory power in the different solutions is in all cases nearly the same. With the menthones separated off, the rotatory power decreases in the same degree as the number of carbon atoms of the acids causing inversion increases. In order to ascertain whether the inversion effected resulted actually from the action of the solvent or merely from heating the menthone, the latter substance was heated alone for three hours in an oil-bath up to 130 to 140°, however, with but little effect on its rotatory power.

When heating *l*-menthone dissolved in acetic anhydride, apparently only small amounts of dextrorotatory isomerides were formed.

Amongst the aliphatic acids, formic acid holds an exceptional position, since it causes inversion already at ordinary temperature. The solution undergoes a gradual change in the rotation which is now generally termed "mutarotation". With c = 12.699 and l = 1 dcm., $[\alpha]_{red}$ amounted, after 2 minutes' action, to −17.42°, after 10 min. −17.25°, 50 min. −15.99°, 120 min. −12.91°, 240 min. −9.53°, one day +10.55°, 3 days +21.42°, 7 days +21.73°. After getting constant, $[\alpha]_r$ was +25.20°.

Opposite to the action of the other organic acids, formic acid, in the authors' opinion, acts principally owing to its dissociating power. Even in diluted solution this acid causes gradual inversion.

In order to prove a possible mutarotation of other terpene ketones when treated with formic acid, *d*-carvone and *d*-fenchone were dissolved in the latter acid, no inversion, however, in the rotation taking place in the course of time. With fenchone, even after 5 day's action, no turning of the rotation was observable; anyhow, a strong influence of the formic acid was noticeable insofar that a considerable rise in the specific rotation was caused by that acid. For instance, pure fenchone rotates, in red light, +46.67°, in formic acid solution +62.38°. Such a rise by action of a solvent has hitherto not been observed with any other ketone examined.

When boiling *l*-menthone in formic acid solution, the value of the rotation is not much higher than the rotation observed at ordinary temperature, when the mutarotation has come to an end.

Furthermore, *l*-menthone was dissolved in concentrated sulphuric acid, and this solution also showed mutarotation. Since the solution turned very dark, the rotatory

dispersion could not be measured, only the final value observed in yellow light was read off: $[\alpha]_D = +38.30°$.

With sulphuric acid monohydrate, *l*-menthone showed such an intense brown coloration and rise in temperature that no optical readings could be taken. Likewise, *d*-carvone and *d*-fenchone turned instantaneously brown in sulphuric acid solution, rendering examination impossible.

On dissolving a dextrorotatory menthone in sulphuric acid no mutarotation was to be observed. This result is opposed to the observations made by Tubandt in alcoholic solution. The last-named author had even established that the inversion of "*d*-menthone", by means of sodium ethoxide in alcoholic solution, proceeds with the same velocity as with *l*-menthone. In alcoholic solution, the *d*-menthone seems to react differently. The proposition advanced by Tubandt: "The inversion of menthone is a reversible, monomolecular reaction caused by acids as well as by bases", must, in the authors' opinion, be altered insofar that it holds not good for alcoholic solutions.

It was most striking that *l*-menthone, when dissolved in bromoform, likewise revealed mutarotation, this phenomenon proceeding even more speedy than in formic acid solution. With chloroform, no changing of the rotation, after some time, was noticed. Hence, the inverting action of bromoform on menthone might be easily made use of for proving the presence of bromoform in chloroform. The bromoform used was quite neutral. With carvone, it caused no changing of the rotation. Bromobenzene causes no alteration whatsoever in the rotation, bromal, however, produced inversion, which the authors ascribe to its acid reaction.

Solutions of *l*-menthone in alcoholic potassium hydroxide showed instantaneously dextrorotation, but the latter did not alter on standing. *d-Iso*menthone ($[\alpha]_D +24.15°$), when dissolved in alcoholic potash, likewise showed no alteration after some time.

d-Carvone and *d*-fenchone turned at once dark when treated with the last-named solvent, thus rendering examination impossible.

In alcoholic hydrochloric acid, *l*-menthone showed no mutarotation, dextrorotation taking place instantaneously.

On boiling with pyridine the rotatory power of *l*-menthone was hardly altered. Likewise, higher boiling bases, *e. g.*, aniline, neither caused inversion, nor did prolonged boiling with toluene result in any alteration of the rotation of *l*-menthone.

Basing on these observations, Grossmann and Brauer consider it doubtful whether the inversion resulting from heating pure menthone is caused, as Beckmann believes, by the action of glass. With the object to study the behaviour of pure *l*-menthone on heating, the ketone was boiled, in a round-bottomed flask of Jena glass, under a reflux condenser. Even after 24 hours' boiling, no alteration of the rotation was to be observed, and equally with dextrorotatory menthones the value of the rotation remained practically unchanged after prolonged heating. Likewise, the optical rotation of *d*-carvone underwent, after prolonged boiling under a reflux condenser, only a very slight alteration, a fact proving that carvone does not pass over into carvacrol so quick as is generally assumed[1]).

In addition, the authors examined the rotatory dispersion of the dextrorotatory menthones in alcohol, benzene, and pyridine. These solvents acted insofar differently from *l*-menthone on dextrorotatory menthone, as they caused a rise of the specific rotation, and not, as with *l*-menthone, a lowering.

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[1]) Comp. T. M. Doormaar (*Chem. Zentralbl.* **1905**, I. 678), who equally investigated this intramolecular rearrangement by heat, yet not polarimetrically, but by determining the specific gravity.

The intramolecular rearrangement produced in menthone by heating may be best explained, as the authors believe, by assuming that a part of the menthone, with change in its configuration, passes over into its enolic isomeride, until a certain equilibrium is reached. It was, however, impossible to indicate, with any degree of certainty, how much of the menthone present undergoes this change.

The inversion of *l*-menthone by aid of certain solvents seems, in Grossmann's and Brauer's opinion, to depend on the additive and the substituting action of the solvent; the intermediate bodies, being probably stable only when dissolved, pass over, by scission, into dextrorotatory menthone by means of a sort of Walden rearrangement.

Finally, the authors express the opinion that all investigations carried out hitherto seem to point out that the influence of the solvent on the optical rotation of active bodies is due to reactions between solvent and dissolved body, for which changes the alteration of the rotation is a particularly sensitive indicator.

A paper by T. Jona[1]) deals with the *cryoscopic behaviour of fenchone*. The cryoscopic constant of this ketone was determined from the depression in the congealing points of substances which generally show a normal behaviour in this respect; while be investigated the association with other compounds by aid of the constant thus derived. The cryoscopic constant of fenchone amounts to 68 and is remarkably small compared with that of camphor (490). The latent heat of fusion is calculated therefrom to be 22.86 calories. According to the generalized rule of Trouton the latent heat of evaporization for fenchone is calculated to be 75.34 calories, a value being in good accord with the constant 73 calculated from the value found from the raising of the boiling point. The molecular depression of the congealing point of the alcohols in fenchone is already, in low concentrations, somewhat below the normal value and decreases still more the higher the concentration rises. With the phenols, the molecular depression is abnormally low in low concentrations, with increasing concentration the value increases likewise. Acids behave in this respect like the alcohols, with exception of salicylic acid, which reacts in this regard as a phenol.

The depression of the congealing point was determined for camphene, camphor, thujone, ethyl acetate, methyl salicylate, benzyl alcohol, benzaldehyde, anisic aldehyde, and a number of other bodies in which we are not interested.

It may be added that Jona prepared the fenchone used in his experiments from fennel oil by treatment with nitric acid and subsequent crystallization, and purified it from camphor by means of its semicarbazone. The abstract at hand does not quote the constants of the fenchone thus purified.

A publication by Th. M. Lowry and H. H. Abram[2]) entitled, *The rotatory dispersive power of organic compounds. Part IX. Simple rotatory dispersion in the terpene series*, deals with a purely physical subject. The paper is not suited for a short abstract, so we content ourselves to mention that the rotations of a number of compounds of the terpene series, including methylene camphor derivatives, camphyl carbinol, menthol and its esters, myrtenol and its esters, and hydrocarbons derived from citronellal, may be expressed by means of the dispersion formula:— $\alpha = k/(\lambda^2 - \lambda_0^2)$. Pulegone and several other bodies show complex rotatory dispersion.

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[1]) *Gazz. chim. ital.* **47** (1917), II. 87; *Chem. Zentralbl.* **1918**, II. 121. — [2]) *Journ. chem. Soc.* **115** (1919), 300.

Botanical Notes.

A new aromatic fungus. — We have repeatedly discussed articles on the smell of fungi[1]) and would now mention a treatise by F. Bataille and L. Joachim[2]), containing a description of a new *Cortinarius* species, *C. suaveolens*. Bataille et Joachim. It has been discovered in the woods of Fontainebleau and is related to *C. calochrous* and *C. dibaphus*. both odourless, whereas this new species has a strong odour of orange blossom, which remains until the fungus is quite dried up. *C. suaveolens* distinguishes itself also in other ways from the other two species named, as may be deducted from the description and illustrations in the original.

As to an attempt to distinguish the physiological forms of the bay-tree, see page 7 of this *Report*.

Phyto-physiological Notes.

A publication by A. Willstätter and A. Stoll[3]) contains noteworthy communications on the isolation of peroxidase from horse-raddish. Although it is not known, whether this peroxidase acts a part in the formation of the essential horse-raddish oil, we wish to discuss the treatise, as it gives an example of the methods by which such sensitive substances have to be isolated. It is not at all impossible that quite a number of essential oils are formed by decomposition of glucosides or such-like bodies, under the influence of enzymes or other substances acting as catalysts. We would mention for instance wintergreen oil, bitter almond oil, &c. These glucosides have not been isolated so far and little is known as to the enzymes.

Willstätter and Stoll point out that the preparation of the enzymes appears to be very different from the isolation of natural colouring matter, but that these tasks have after all remarkable relations. Peroxydase as well as chlorophyll are substances which, for lack of groups capable of reacting, do not offer any points of attack in order to isolate them chemically. Both are sensitive against acids, and although they do not possess any basic properties they are attacked by acids to such a degree, that all the active groups are destroyed.

The concentration of the enzymes in the plant is more unfavourable than with the pigments. The contents of peroxydase amounts to only 0.035 in fresh and to 0.14 per cent. in dried horse-raddish, whereas for instance chlorophyll constitutes 0.2 per cent. of the fresh and 1 per cent. of the dried leaves.

There are three important points with regard to the preparation of the peroxydase, which we only wish just to mention.

1. Dialysis in the plant material. During this process about 20 per cent. of the enzyme is lost.

2. The adsorption in the plant material when treating with oxalic acid. This operation is carried out with a carefuly ajusted quantity of oxalic acid, as an excess thereof would destroy the peroxydase. The slices of horse-raddish root are placed into the dilute acid for 4 to 6 hours. As in this treatment the regulating action of the live protoplasm is paralyzed and that of the enzyme set free, the resolution of the formerly protected bodies begins; mustard oil is set free in considerable quantity, as otherwise through grating.

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[1]) Comp. for instance *Reports* October **1916**, 100; October **1918**, 108. — [2]) *Bull. Sciences pharmacol.* **25** (1918), 350. — [3]) *Liebig's Annalen* **416**, (1918), 21.

3. Fractionated extraction with alkali. The peroxydase can be extracted from the root pulp only after complete saturation of its acid content. Under the influence of baryum hydroxide until the reaction is neutral, accessory acid substances are carried off with the first extract. Afterwards, the plant material takes up a considerable additional quantity of baryta, until the enzyme passes over into the feebly alkaline water.

The authors indicate a fairly exact method for judging the concentration of the peroxydase solution, but it would lead us too far to describe it.

The formation of fatty and essential oils in the plant. — According to J. Dufrenoy[1]) neutral fats and essential oils are formed in the same way in the interior of the chloroleucytes, but at the expense of the nucleus. They can replace each other as degeneration products of the cell or may occur side by side. The tissues in the course of degeneration show a pronounced general chromatophily. The amyloleucytes disappear from the cells, in which the fats collect. The glucosides do not diminish. The fatty degeneration is a general cell phenomenon which the animal and vegetable cells have in common.

As to a new bacteria disease of the *Citrus* species, see page 27 of this *Report*.

Regarding the treatment of peppermint rust, see page 40 of this *Report*.

Physiological and Pharmacological Notes.

Some years ago, we discussed H. Teudt's[2]) *theory of the origin of the phenomena of smell*. Since then, the author has further developed his theory and reported on it elsewhere[3]). He starts from the observation, that with all chemical compounds which have an odour, this cannot be modified as long as the molecule is not destroyed. From this he concludes that the hitherto unknown cause of the smell cannot be outside of, but must be in, the molecule. Then, it is true, the question remains still unanswered, whether it is to be looked for in, or outside of, the atoms. Conjecturing further, he comes to the result that the cause of the formation of smell must lie between the atoms in the molecule. The only substantial matter between the atoms in the molecule being the valency electrons, the cause of smell would have to be looked for there. The molecules of odorous substances do not undergo any change owing to the emanation of odour, so that he takes it that smells are caused by movements repeated over and over again in the same way, *i. e.* by vibrations of the valency electrons. In this case, one must also take it for granted that there are similar vibrations in the olfactory nerves of the nose.

What is new in his present publication is a speculation about the origin of the vibrations of the valency electrons inside the molecules so as to produce smell, which he tries to make clear through several figures. A reproduction thereof and a detailed discussion would lead us to far and we would only mention some of the chief points.

He arrives at the conclusion that, if the smells are brought about through vibrations of the valency electrons, a chemical element can form odorous compounds all the more easily, the firmer its electrons are bound to the nucleus of the atom. According to his theory, the atoms of metals are not fit to produce the vibrations necessary for

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[1]) *C. r. de biologie* **81** (1918), 920; *Chem. Zentralbl.* **1919**, I. 659. — [2]) *Biol. Centralbl.* **33** (1913), 716; *Report* April **1914**, 123. — [3]) *Prometheus* **30** (1919), 201, 209.

the development of smell, as their electrons can easily be shifted. In fact, the simple compounds of all the metals are inodorous, and if some complicated organic compounds of metals have a smell, it is not produced by vibrations of the valency electrons between the metal atoms, but by the vibrations of those between other atoms of the molecule.

With the aid of his theory, he then explains the inodorousness of various bodies, such as methane, ethane, &c. As to the transmission of smell, he says that the molecules of the air take the smell, so that a volatilization of the smelling body itself would not be necessary. So far the contrary has been believed, although it was difficult to make this supposition agree with the fact that it was impossible to prove any loss of weight with many strongly smelling substances, even if they had filled large rooms with their odour for some length of time. A further point against the old theory would be that the smell of less volatile substances are in may cases spread much farther and much more intensely by currents of air, than those of very volatile bodies. The author mentions, besides, that certain animals can scent the smell of man from a distance and that it is recognized by dogs days afterwards in the footprints. If this smell was caused by odorous matter, separated from the human body, it is Teudt's opinion that this substance, on the one side, would have to be rather heavy so as to prevent its being carried away, whereas on the other side it would have to be light, in order to be carried far off by the wind. This contradiction was to be solved with the aid of his theory, according to which the vibrations of the smell of man are taken up the same by those air molecules carried away by the wind, as by those clinging to the soil, owing to adhesion.

Teudt points out that the vibrations produced in the air molecules by odorous substances make themselves conspicuous by changing the physical behaviour of the air, in that its power of absorption for radiated heat is considerably increased by conducting it over smelling bodies. According to Tyndall's[1]) experiments, patchouly increased 30 times and anise even 372 times the power of absorption of ordinary dry air, without the air having taken up any ponderable quantities of these substances. This phenomenon, unexplained so far, comes about, according to Teudt, through the destruction of part of the heat rays, because they interfere with the vibrations of the electrons produced in the air molecules by odorous bodies. Teudt further succeeds in explaining, with the aid of his theory, the fact that, with many homologous ranges of organic compounds, the quantities which it is possible to notice decrease with increasing molecular weight, but we must refer our readers to the original for more particulars.

"*Der Duft als analytisches Kennzeichen*" (Smell as an analytical mark of distinction) is the heading of an article by H. Heller[2]), with the contents of which we agree throughout. The author lays stress upon the fact that, in the description of chemical bodies, the smell is generally not mentioned, unless it is specially remarkable. He ascribes this to the disinclination of chemical men to indicate as characteristic in every case such properties as are more or less subjective and cannot be expressed by figures. Those, however, whose domain is the chemistry of the aromatics, are of a different opinion and assign to the smell the same importance as to the colour and, to a certain extent, that of the data expressible in figures. For instance, the characterization of compounded flower oils with physical data is difficult, if not impossible, as long as not all the

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[1]) The heat, looked upon as a kind of motion, 1875, p. 411, &c. — [2]) *Deutsche Parf.-Ztg.* 5 (1919), 91.

constituents are known. In this case the judgment must be left to the sense of smell. The fact that the scientific language has not coined so far any concise unequivocal terms for scents is certainly one of the chief causes of so little value being attributed to smell in the descriptions especially of new bodies, unless they are aromatics proper. However, this very same uncertainty existed until a very short while ago also with regard to the designations of colours. For the time being, this lack of a scientific nomenclature of smells cannot be remedied, as one has only just begun to lay the foundations based on experience. This is a consequence of so little having been communicated about the odour of all the bodies, so that the systematizer is forced to make up for what has been neglected, to determine by himself the tremendous variety of smells, to classify them and, if possible, to introduce general terms.

In connection with this publication, we would mention an article by H. J. Prins[1]), published some time ago, and select from it what we think would chiefly interest our readers. This author likewise mentions that, generally speaking, far more value is attached to the colour of new chemical bodies than to their odour. In his view, the human nose is less developed than the eye, so that it has happened that bodies have been described a long time ago, without discovering their aromatic nature. Phenyl ethyl alcohol, for instance, known since about 1880, has been used as an aromatic only after it had been discovered that it is an important constituent of otto of roses and is of great value for its smell[2]). The odour of this body, as well as that of cinnamic alcohol, so important for perfumery, and of other important alcohols is described in G. Cohn's book *(Die Riechstoffe)*. published in 1904, as so weak that they are termed of no value as aromatics.

Phenyl ethyl alcohol is an instance also for the phenomenon that aromatics are modified by traces of impurities to such an extent, that it is almost impossible to recognize their true odour. It is necessary therefore that aromatics are not only chemically pure, but also pure in smell, which is still more difficult to attain than chemical purity. This can be explained by the fact that there are scarcely any combinations in colouring matter which are offensive to the eye, whereas in smells it very frequently happens with regard to the nose. Perhaps this is only a matter of habit; our modern combinations of colours are far more daring than the old ones, the same as we encounter in modern music harmonies and disharmonies which are far rarer in classical music. It is not impossible, in consequence, that man, with further development of his olfactive organ, may discover more harmony in combinations which we now still call disagreeable.

The author then briefly discusses the work done by Zwaardemaker and Hennig and the publications of Klimont, Rupe and Majewsky and Marchand, all discussed already in our *Reports*. and gives examples for similarity or difference of smell with similarity or dissimilarity of chemical construction.

If for instance the constitution of an aliphatic aldehyde is altered by isomerization of the hydrocarbon residue, the influence upon the smell is the greater, the more considerable the chemical influence of the isomerization is upon the aldehyde group. In consequence, there is a considerable difference in smell between laurinaldehyde and

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[1]) *Handelingen van het XVIe Nederlandsch Natuur- en Geneeskundig Congres, gehouden op 12, 13 en 14 April 1917 te 's-Gravenhage. Sub.-Sect. Scheikunde, S. 205.* — [2]) In this connection, we would also mention methyl anthranilate, known for a long time before it was used in the preparation of artificial flower oils, which was done only after it had been discovered in neroly oil. Comp. *Report* **1895**, 72; Walbaum, *Journ. f. prakt. Chem.* II. **59** (1899), 350.

methylnonylacetaldehyde. The elimination of an ethylene linking of the aldehyde group influences the smell to a great extent. For example, there is but little difference in the smell of decyl and undecylenaldehyde (double linking in 9, 10-position), whereas it is quite marked between nonylaldehyde and α,β-nonylenaldchyde, as well as between caprylethyl ester and heptincarbonethyl ester (acetylene linking in α,β-position). The difference in smell is likewise considerable between citronellal and citral, less so between citronellol and geraniol. In the case of cyclic compounds, the position of the double bond is of influence upon the smell, for instance with α- and β-ionone, in the latter of which there are conjugated double bonds, but not in the former.

For further instances, we beg to refer to the original.

Th. H. Durrans[1]) has published an extensive treatise *on the relations between odour and chemical constitution*. He has studied quite specially the compounds composed of carbon, hydrogen and oxygen. For most of the numerous bodies mentioned by him, he has been compelled to cull from previous publications the notes regarding smell, which for the reasons stated before are not very reliable.

In the introduction he points out that the smell of most bodies has been judged at ordinary temperature, whereas the degree of volatility is decisive in many cases for the fact, whether a substance smells or not. Inodorousness is sometimes caused by insufficient vapour pressure. Most likely chemical bodies like ether, ethyl acetate and acetone are inodorous at a low temperature and perhaps all compounds have no smell if the temperature be sufficiently low[2]). G. Woker's supposition[3]) that smell depends upon volatility is not correct, according to Durrans, for it does not agree with the fact that high-boiling compounds with consequently low vapour pressure at an ordinary temperature, such as coumarin, santalol, muskone, &c., smell quite specially strongly.

Durrans further discusses the fact that there does not seem to be any connection between smell and colour, although some bodies exist, like quinone and chromane, which smell strongly and are coloured intensely at the same time.

After a critical review of previous publications on the connection between smell and chemical construction, the author gives a systematic summary of the odoriferous properties of aliphatic, aromatic and hydroaromatic hydrocarbons, saturated and unsaturated aliphatic alcohols, aromatic alcohols, hydroaromatic alcohols, phenoles, aliphatic and aromatic aldehydes, aldehyde hydrates and acetals, ketones, ketenes, polymethylene ketones, acids, esters, acid anhydrides, ethers and oxides, in all about 1000 chemical bodies. A full report on his consecutive theoretic reflections would lead us too far, so that we shall only extract some particulars

With aliphatic hydrocarbons, the acetylene linking, as a rule, produces a disagreeable smell, which is not the case with aromatic hydrocarbons. Hydrogenization of the benzene ring has a considerable effect, which is the greatest if two hydrogen atoms are added; with the naphthalene ring, the effect is quite the opposite. With aliphatic alcohols, the same as with many other types of compounds, the intensity of smell rises with the number of carbon atoms, reaching its maximum at C_{10}. A tertiary carbon

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[1]) *Perfum. Record* **10** (1919), 104. — [2]) From a theoretical point of view, it is very important to know, whether a substance which at ordinary temperature is inodorous would become odorous at a higher temperature, *i. e.* with increasing vapour pressure. This will have little importance, however, for practical purposes, as most aromatics are used only at an ordinary temperature. — [3]) *Journ. of physic. Chem.* **10** (1906), 455; *Report* April **1907**, 113.

atom causes a camphorlike odour, most distinct, if it is located next to the hydroxyl. The tertiary carbon atom does not produce a camphorlike smell in aromatic alcohols, but in hydroaromatic ones, especially if the tertiary carbon atom is close, or in para-position, to the hydroxyl group. The polyatomic alcohols are mostly inodorous, but a tertiary carbon atom may, if connected with the hydroxyl, cause a camphorlike odour. In the case of phenoles, tertiary carbon does not produce any camphorlike smell. Hydrogenization of the benzene ring in phenoles alters their smell altogether; the substitution of the hydroxyl hydrogen brings about a strong modification of smell. α-naphthol ethers are inodorous, but become odorous on hydrogenization. The aldehyde hydrates have an intense odour and alkylization of the hydroxyl produces a tremendous change in it. With aliphatic ketones the smell begins suddenly with the 8th carbon atom, the climax being reached with a normal C_{11}-chain. The odour is considerably intensified by ethylene linkings. A tertiary carbon atom generally produces a camphorlike smell, whereas it is of no consequence with acetophenones. In the case of polymethyl ketones, the characteristic smell cannot be ascribed to special causes. With saturated monocarbon acids, the smell disappears with the C_{14}-homologue. Polybasic acids are all inodorous. There is the same gradation with the esters of aliphatic acids, as with the alcohols and acids; however, inodorousness does not begin suddenly with the C_{14}-homologue. With lactones, the tertiary carbon atom does not always bring about a camphorlike smell.

Finally, Durrans discusses the different theories with regard to smell, the influence of molecular weight, of ring closing, and of partial valencies, arriving at the conclusion that there is sufficient reason to believe that the smell is primarily caused by the presence of free partial valencies.

On a previous occasion, we discussed an interesting investigation of K. v. Frisch[1]) on the *sense of smell in bees* and its importance with regard to their visiting flowers. Since then, a second publication of the same gentleman has appeared on the subject[2]). According to Sprengel's theory, the scent of the flowers attracts the insects, a view that has scarcely been questioned by anybody. Just this unanimous assent to it may be the cause, von Frisch thinks, that we know so remarkably little up to now about the importance of the scent of flowers for their fertilization. It has been the aim of the author's experiments, continued for several years, to fill up this gap at least in part.

He experimented exclusively on the honey-bee. The order of the experiments with the aid of cardboard and earthenware boxes has been described already in the first publication. The latter have the advantage over the former of being inodorous; besides, they can be used again after having been cleaned. The results of the experiments, described already before, show clearly that the smell of the flowers guides the bees when in search of nectar.

In order to be able to appreciate justly the importance of the flower scent, von Frisch trained his bees to find out a certain smell (in this case that of Messina Orange oil)[3]) among numerous different smells. For this purpose he put 24 boxes in two rows, one on top of the other; 23 were without scent, whereas the bees were fed

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[1]) *Verhandl. der K. K. zoologisch-botanischen Gesellschaft*, Vienna **65** (1915), number 1 and 2; *Report* October **1917**, 127. — [2]) Lecture given on March 15th 1918 at the meeting of the zoological section; *Verhandl. der K. K. zoologisch-botanischen Gesellschaft*, Vienna **68** (1918), 129. — [3]) The author does not say whether he used sweet or bitter orange oil.

in the remaining one, previously perfumed with the oil in question. When carrying out the experiment, he replaced all the boxes by others, one of which contained the training perfume, whereas in the others 23 different scents had been used. This experiment was repeated, when again 23 different scents were offered in addition to that, upon which the bees had been trained. The author watched for 5 minutes how the boxes were frequented and obtained the following results:—

1. Oil of orange peel, Messina (1st experiment)	205
2. Limette oil	148
3. Oil of orange peel, Messina (2nd experiment)	120
4. Bergamot oil	93
5. Oil of orange peel, Spanish	60
6. Spike oil	8
7. Orange blossom (Extr. quadr.; alcoholic extract from pomade)	7
8. Cajuput oil	5
9. Orris oil, liquid	5
10. Lavender oil	5
11. Thyme oil	5
12. Marjoram, cultivated	4
13. Myrtle oil	4
14. Fennel, sweet	3
15. Patchouly oil	3
16. Rose (Extr. quadr.; alcoholic extract from pomade)	3
17. Eucalyptus oil	2
18. Geranium oil (Grasse)	2
19. Peppermint oil	2
20. Tuberose (Extr. quadr.; alcoholic extract from pomade)	2
21. Basil oil, sweet	1
22. Citronella oil	1
23. Fennel, bitter	1
24. Marjoram, wild	1
25. Savin oil	1
26. Verbena oil	1
27. Bitter almond oil, genuine	0
28. Cassie flower oil	0
29. Cassie (Extr. quadr.; alkoholic extract from pomade)	0
30. Cypress oil	0
31. Tarragon oil	0
32. Geranium oil, Réunion	0
33. Cucumber oil	0
34. Jasmine flower oil	0
35. Jonquille (Extr. quadr.; alcoholic extract from pomade)	0
36. Irisine	0
37. Cherry-laurel oil	0
38. Clove oil	0
39. Orange flower oil	0
40. Reseda (Extr. quadr.; alcoholic extract from pomade)	0
41. Rosemary oil	0
42. Sandalwood oil	0
43. Celery oil	0
44. Mustard oil	0
45. Staranise oil	0
46. Tuberose flower oil	0
47. Juniper berry oil	0
48. Cassia oil	0

These tables show that the bees found out with remarkable certainty the smell upon which they had been trained and those closely allied to it, which entitles one to the conclusion that they use their faculty of distinguishing between different smells also in the selection of the flowers. On the other hand, the author lays stress upon the fact that the bees did not distinguish with certainty between the training perfume and some others which, although there is a similarity with the training perfume, can be recognized or even distinguished clearly by the olfactive sense of man.

There are, however, chemically well defined aromatics, the smell of which appears similar to the human nose, although they differ considerably in chemical composition. If such scents were confounded too by the bees, it would point to a certain conformity with regard to the physiological foundation of perceiving smells in man and bee, which is not at all selfevident in view of the different build of the olfactive organs. The results of exhaustive experiments with such couples of aromatics which in spite of

different chemical composition seem to us similar in smell show in fact, that there also seems to exist a certain similarity of smell for the bees, although there were exceptions. Nitrobenzene and bitter almond oil, for example, were confounded, whereas the bees clearly distinguished between *iso*-butyl benzoate and amyl salicylate, which the human nose does not distinguish. von Frisch comes to the conclusion that, with the bee as with human beings, the arrangement of the atoms in the molecule is of importance with regard to the quality of smell.

Comparitive experiments were also carried out as to the action of odour and colour. The bees were trained upon smell and colour, by feeding them in a box perfumed with mignonette and the front of which was covered with blue paper. The two factors were put into competition, by using two boxes, one perfumed with mignonette, but colourless; the other inodorous, but blue. The bees examined both, but generally speaking the scented box was more frequented than the coloured one, the scent therefore having the greater effect. In one point, however, the colour was superior to the smell, as it acted at a longer distance.

In order to determine the intensity of the smelling power of the bees, experiments were made with tuberose oil, bromstyrol and methylheptenone. The bees were trained upon the respective smell, which was then presented to them in ever increasing dilution, until they no longer preferred the scented box to the unscented one. The limit of perceptibility for the three scents in question agreed fairly well with that for a normal human nose. The limit found remained the same, even if the bees had been trained upon another concentration of smell, which proves that this limit is independant of the concentration originally chosen. The intensity of smelling power of the bee does not seem to be very different from that of man and is at least of equal magnitude.

von Frisch has not been able to confirm the assertion that bees scent nectar and honey from great distances. If it was the case, the sense of smell of the bee would in this respect be vastly superior to that of man. The observations which induced some authors to suppose a long-distance action of the honey odour, are explained, according to von Frisch, by the assumption that honey odour is in the main nothing else but flower scent absorbed by the nectar.

The possibility that bees might be able to perceive odours, for which we are not susceptible, seemed to be realized in the flowers of Virginia creeper *(Ampelopsis quinquefolia)*, but all the author's relative experiments did not show any result. The flowers of Virginia creeper are scentless, the same for the bees as for us.

Further experiments, which von Frisch undertook in order to decide the question, up to what degree the bee is capable of finding out the training scent in a mixture, showed that a rather inconsiderable admixture of a different flower smell strongly diminished the attractive effect of the former.

As to the biological importance of the flower scent, it is quite correct, according to von Frisch, that it is a bait for insects, especially for flies, beetles and some butterflies. Of considerable importance is the fact that the profusion of different smells, characteristic for the species of plants, enables the bees and other insects to distinguish the flowers sought after from those of other kinds and to facilitate the recognition of flowers of the same kind. The odour of the flower, therefore, is a distinctive mark for the bee, perhaps the most important that the flower has.

von Frisch then discusses some experiments, the results of which are important with regard to the psychology of the bee.

The success of training the bees upon all the flowerlike scented substances had been fairly easy, but similar experiments with the foul-smelling scatole failed. It seemed that the smell of scatole had nothing repulsive for the bees, for they entered without hesitation the scatole boxes, in which they were fed. If the task was set them to find out an empty box, scented with scatole, among other, unscented, empty boxes, they showed great uncertainty and did, as a rule, not frequent the scatole box any more than the inodorous ones. Nevertheless, the bees perceive the smell of scatole, for, if bees trained upon orange blossom perfume have to chose between two boxes, of which the one contains only orange blossom oil and the other, in addition to a similar quantity of orange blossom oil, some scatole, they prefer the former.

There were positive results with patchouly oil, it is true, but also with this aromatic the bees showed uncertainty. The bees perceive the smell of scatole and patchouly oil, but they do not learn at all, or only incompletely, that the presence of these bodies may mean food. This was the case only with such odours as are unknown to the bees from nature and have not the slightest resemblance with those which since uncounted generations are of importance for the bees collecting honey.

In this connection, it is remarkable that training them upon lysole succeeded very well.

According to von Frisch, it results that the olfactive sense of the bee is not so widely different from that of man, as might have been expected in consequence of their unlike organization.

Über Duft und Geruch (About Odour and Smell) is the title of an article by H. Heller[1]), which contains reflections worth reading on the two terms in question and many other interesting views. It does not lend itself, however, to a short review.

A. Koelsch[2]) has published an article on the Biology of the Odour of Plants. We need not go into it any further, for it deals only with J. Giglioli's work on the subject. The uninitiated reader might conclude from the article that the observations mentioned were quite new, but this is not the case, as Giglioli's relative studies have been discussed on page 162 of our April *Report* 1912.

We wish to add to our discussion of A. Durand's treatise on the theory of smelling[3]) that the supposition of ionized molecules would afford perhaps an explanation of the property of aromatic particles, observed by the author, to condense water vapour when they are in a gaseous state.

In order to judge the antiseptic power of some essential oils, L. Cavel[4]) studied their action on ordinary beef-tea, which he had previously infected with water taken from the collecting tank of a sewerage system. Other authors (Cavel only quotes older French scientists, it is true) had always studied the action of only one kind of bacteriæ, whereas Cavel investigated so to speak the general antiseptic action, for similar water contains a great variety of microbes, mostly saprophytes, but also some pathogenetic germs.

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[1]) *Prometheus* **1918**, Nos. 47/48; *Deutsche Parf.-Ztg.* **5** (1919), 2. — [2]) *Deutsche Parf.-Ztg.* **4** (1918), 174. — [3]) *Report* April/October **1918**, 128. — [4]) *Compt. rend.* **166** (1918), 827.

He determined for every oil the dilution, at which it no longer showed any antiseptic effect, arriving at the following limits of concentration: —

Thyme oil	0,7 : 1000	Mustard oil	4,2 : 1000
Origanum oil	1,0 : 1000	Rosemary oil	4,3 : 1000
Portugal oil	1,2 : 1000	Cumin oil	4,5 : 1000
Verbena oil	1,6 : 1000	Neroly oil	4,75 : 1000
Cassia oil	1,7 : 1000	Lavender oil	5,0 : 1000
Rose oil	1,8 : 1000	Balm oil	5,2 : 1000
Clove oil	2,0 : 1000	Ylang-Ylang oil	5,6 : 1000
Eucalyptus oil	2,25 : 1000	Juniper berry oil	6,0 : 1000
Peppermint oil	2,5 : 1000	Fennel oil, sweet	6,4 : 1000
Geranium oil (Rose de France)	2,7 : 1000	Mignonette oil	6,5 : 1000
Vetiver oil	2,7 : 1000	Garlic oil	6,5 : 1000
Bitter almond oil	2,80 : 1000	Lemon oil	7,0 : 1000
Gaultheria oil	3,0 : 1000	Cajuput oil	7,2 : 1000
Geranium oil, Indian	3,1 : 1000	Sassafras oil	7,5 : 1000
Wintergreen oil[1])	3,2 : 1000	Heliotrope oil (?)	8,0 : 1000
Spiræa oil (Reine des prés)	3,3 : 1000	Limes oil	8,4 : 1000
Spike oil	3,5 : 1000	Turpentine oil	8,4 : 1000
Staranise oil	3,7 : 1000	Parsley oil	8,8 : 1000
Orris root oil	3,8 : 1000	Violet oil	9,0 : 1000
Ceylon Cinnamon oil	4,0 : 1000	Camphor oil	10,0 : 1000
Snake root oil	4,0 : 1000	Angelica oil	10,0 : 1000
Birch oil	4,8 : 1000	Patchouly oil	> 15,0 : 1000
Anise oil	4,2 : 1000		

The limit for phenole was 5.6 : 1000.

The older authors mentioned by Cavel, as stated before, are Jalan de la Croix[2]), Chamberland[3]) and E. de Freudenreich[4]).

We would add that many others have of late studied the disinfecting action of essential oils and aromatics, such as Calvello[5]), Marx[6]), K. Kobert[7]), W. M. Martindale[8]), R. Geinitz[9]) and others.

Physiological action of the mustard seed oils. — Mustard seed oils being, as it is known, bodies of violent smell and sharp taste, it is quite interesting to get to know something about their physiological action.

W. H. Peterson[10]) investigated the alteration of mustard oils, *i. e.* not only the ordinary allyl mustard oil, but also allyl sulphide, in the assimilating process of pigs, when fed with starch, salts and cellulose. The daily addition of 0.2 to 0.4 gram of mustard oil and 0.5 to 1.0 gram of allyl sulphide caused a gradual rise in the total sulphur content of the urine, which kept on for 10 to 12 days after the administration had ceased, a sign of how slowly the oils were decomposed. The increase was limited to the unoxidized part of the sulphur, whereas there was scarcely any unaltered oil or none at

[1]) Would be identical with gaultheria oil. — [2]) 1881. — [3]) *Ann. de l'Inst. Pasteur* **1** (1888), 153. — [4]) *Ann. de Micrographie* **1889**, 497. — [5]) *Pharm. Ztg.* **47** (1902), 759; *Report* April **1903**, 80. — [6]) *Centralbl. f. Bakteriol. und Parasitenk.* **33** (1903), I. 74; *Report* April **1903**, 80. — [7]) Systematic experiments as to the antiseptic action of essential oils and components thereof. *Report* October **1906**, 155; — *Pharm. Post* **40** (1907), 627; *Report* April **1908**, 174. — [8]) *Perfum. Record* **1** (1910), 266; *Report* April **1911**, 157. — [9]) *Sitzungsberichte und Abhandlungen der Naturforschenden Gesellschaft zu Rostock. Neue Folge* **4** (1912). *Report* October **1912**, 133. — [10]) *Journ. Biol. Chem.* **34** (1918), 583; *Chem. Zentralbl.* **1919**, I. 388.

all. Only if considerable quantities of allyl sulphide had been given, this body was recognizable in the urine by its smell. The excrements did not show any increase of volatile or total sulphur. It is to be presumed that the remainder was secreted by the lungs and the skin.

Treatment of the hook-worm disease with wormseed oil. — Following up our communications on page 61 of this *Report*, we now discuss some further successes obtained with this remedy.

R. L. Levy[1]) reported at the John Hopkins Hospital Medical Society on a case of infection with *Ankylostoma duodenale* and its treatment with chenopodium oil, showing slides at the same time. The patient, a Norwegian sailor, 23 years old, had been taken to the hospital about 8 weeks before, complaining of head-ache, general pains in the body and swelling of the legs. He asserted that he had always been healthy and hard-working and had travelled almost over the whole civilized world. His illness had begun in Mexico about a month before being accepted at the hospital. There he had walked bare-foot for the first time on his journeys. Soon a painful sore place developed on top of the left foot, matter was formed and it was impossible to heal the wound. A short time after the feet and legs began to swell, the patient felt weak, irritable and unfit for work. He went to a hospital in Mexico and stayed there for 3 weeks. Although no medicines were given him there, the swelling disappeared and he was dismissed as convalescent. Twelve days prior to his entering the John Hopkins Hospital, the legs swelled again, the man felt faint, had fever and moderate diarrhœa. On being admitted, the following particulars were stated: Remarkable pallor, fever, tachycarditis, jellylike œdema of the ankles and of the shanks, further a pigmented cicatrice on top of the left foot. The patient was extremely weak and irritable. The blood contained 1660000 red and 6440 white corpuscles, the hæmoglobin content being 25 per cent. (according to Sahli). Besides hyaline and crescent-shaped cells of the parasites of tropical fever were found. Examination of the stools revealed the presence of the eggs of *Trichuris trichiura* and of the hook-worm. It was possible to master the tropic fever soon and the *Trichuris* eggs disappeared after a strong purgation. However, it was impossible to get rid of the hook-worms, although the thymol treatment recommended by the Porto Rico Commission was repeated three times with intervals of a week. The patient was then given chenopodium oil (American wormseed oil), according to the somewhat modified prescription of Schüffner and Vervoort[2]). The patient had to fast for 8 hours and was then given 1 ounce of Epsom salts. Two hours later, 16 drops of chenopodium oil were administered, mixed with a tea-spoonful of granulated sugar. This was repeated twice with two hours' interval. Two hours after the last administration, he was given 1 ounce of castor oil and 50 minims of chloroform. The examination of the excrements of the next 24 hours revealed 19 hook-worms of the "Old World" type. Besides, eggs were ejected continually. For this reason, the same treatment was repeated after 5 days, with the result that 7 more hook-worms were driven off, but no more eggs. In order to make quite sure, the patient was treated once again with woormseed oil, but as the stools did not then contain any worms, he was considered free from intestinal parasites. The increase in weight was 30 lbs., the blood contained 4110000 red and 11000 white corpuscles, the hæmoglobin content (Sahli) being 70 per cent. It was interesting to note the alteration of the proportion of eosinophile cells and white corpuscles, which was

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[1]) *John Hopkins Hospital Bulletin* **25** (1914) No. 279, page 160. — [2]) *Münch. med. Wochenschr.* **60** (1913), 129; *Report* October **1913**, 108.

7 per cent. when the patient was admitted, but later on 36 per cent. The Commission in question considers this rise in the propertion as a favourable prognostic.

In the treatment of hook-worm disease, American wormseed oil shows the following advantages over thymol: —

1. According to Schüffner and Vervoort, the oil is more effective.
2. It is not disagreeable to take.
3. Its administration has no disagreeable after-effects. Stiles and Boatwright have recently pointed out that, with thymol, in more than half of a great number of cases undesirable after-effects were observed.
4. The quantity of oil necessary for the treatment has no toxic effect. Thymol causes occasionally, though very seldom, violent symptoms of poisoning.

We have repeatedly called attention to the successes obtained in treating diseases of the respiratory organs with injections of mixtures of eucalyptole and menthol [1]). H. Strauss [2]) now reports on his experience in this domain. He employed this process according to von Klingmüller and Berliner in seven cases of gangrene of the lungs, obtaining four complete cures. In about 24 cases of pneumonia with delayed loosening, he often had a "favourable impression", whereas he obtained good effects with putrid bronchitis, uncertain effects with acute pneumonia and none at all with *Tbc. pulm.* and pleuritis. The prescription was: —

Rp. Menthol 5.0
Eucalyptole (albiss.) 10.0
in Ol. Dericini (or Ol. Olivar. or 25 per cent. Jodipin or Paraffin. liq.) [3]).

Of this solution he applies 1 to 2 cc. as intragluteal injections. There were only very seldom pains or infiltrations, never any abcesses. Strauss also recommends the rectal application, in which case he gives 5 cc. of the following: —

Rp. Menthol 2.5
Eucalyptole 5.0
Ol. oliv. 2.0
f. emuls. c. Gi. arab. et aq. ad 50.

Strauss thinks this method appropriate too for the local treatment of post-dysenteric proctitides.

Regarding the use of benzyl alcohol as an anæsthetic, see page 66 of this *Report*.

As to the physiological action of panacene, see page 32 of this *Report*.

The preparation of a substitute for mustard powder with the aid of mustard seed oil is mentioned on page 36 of this *Report*.

The pharmacological use of oil of turpentine is discussed on page 53 of this *Report*.

For conservation of chloroform with the aid of i-terpineol, see page 75 of this *Report*.

The use of thymol as a remedy against trichinosis is dealt with on page 75 of this *Report*.

With reference to cases of poisoning with American wormseed oil, comp. page 61 of this *Report*.

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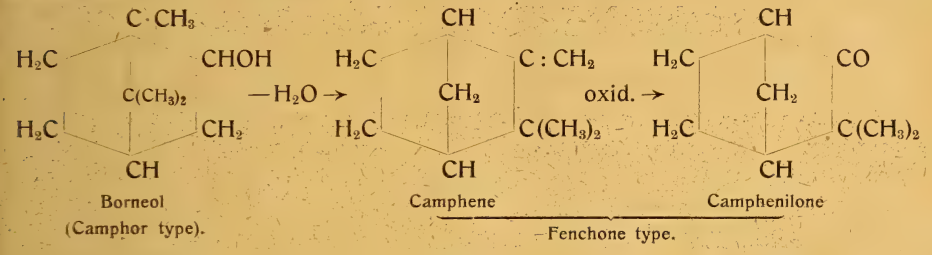
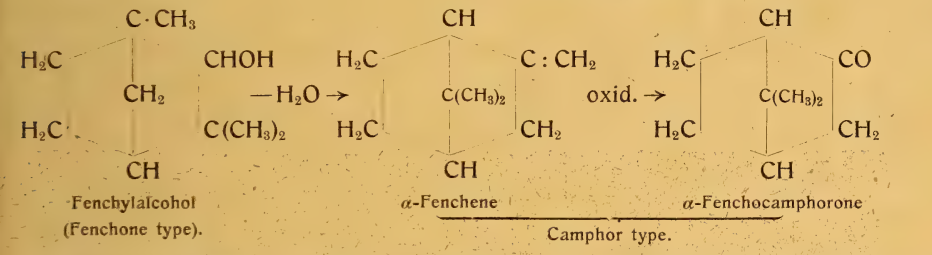
[1]) Comp. *Report* October **1917**, 131. — [2]) *Ther. d. Gegenw.* **1918**, 361; *Therap. Monatsh.* **33** (1919), 74. — [3]) The quantity is not indicated.

Chemical Notes.

For the rearrangements occurring in pentaceanic cyclic systems by splitting off water or hydrogen chloride, L. Ruzicka[1]) suggests the term of *Wagner's rearrangement*[2]), since Wagner was the first to give a correct interpretation of the well-known transposition of this class, *i. e.* the transition of borneol to camphene. This camphene transposition would then be a special case of Wagner's rearrangement.

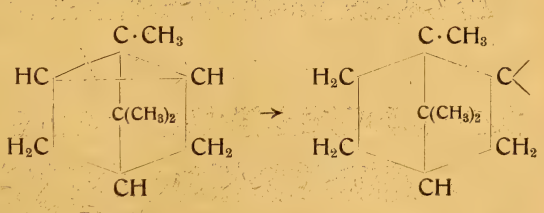
This transposition allows to pass from the "camphor type" to the "fenchone type" and *vice versâ*. as is illustrated by the following formulæ: —





In order to explain the Wagner rearrangement, two assumptions have been made. According to the first, there is primarily formed on abstracting water from borneol an unstable body, *i. e.*. tricyclene[3]); according to the other, a body with a bivalent carbon atom[4]). By splitting one of the linkings in the tricyclic ring, the tricyclene should pass over directly into camphene, whereas the body with the bivalent carbon atom would first have to undergo a rearrangement of the carbon bonds.

The question which of the two explanations is correct, might, in Ruzicka's opinion, be easily solved in favour of the formation of tricyclene in case it would be possible to prove that Wagner's rearrangement occurs also with a tertiary alcohol, since with such a body no bivalent carbon atom can appear. Ruzicka actually succeeded in proving that with methylborneol and methylfenchyl alcohol, obtained from camphor or fenchone according to Zelinski[5]) by treatment with methyl magnesium iodide, the splitting-off of water is connected with Wagner's rearrangement, so that tricyclene must be assumed as intermediate product.



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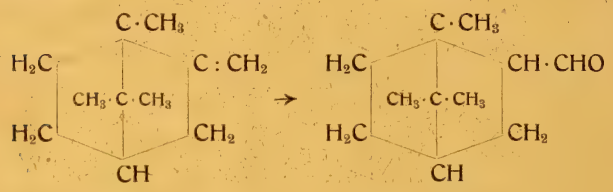
[1]) *Helvetica chimica acta* **1** (1918), 110. — [2]) *Journ. Russ. phys.-chem. Soc.* **31** (1899), 680. — [3]) Comp. Semmler, *Die ätherischen Öle*, Leipzig 1906, vol. III. p. 111. — [4]) Meerwein, *Liebig's Annalen* **405** (1914), 133. — [5]) *Berl. Berichte* **34** (1901), 2877, 2883.

In addition, it is of interest that simultaneously with the occurrence of Wagner's rearrangement with these two alcohols a mutual transition of camphor into fenchone and *vice versâ* is effected which hitherto had not been observed.

Ruzicka mentions furthermore that already Wallach[1]) had investigated the splitting-off of water with methylborneol and methylfenchyl alcohol; yet Wallach termed the hydrocarbon which, on oxidation, yielded camphor, "homocamphene". Since, however, a hydrocarbon belonging to quite a different system is designated as "camphene", it would, in Ruzicka's opinion, in order to avoid confusion, be more correct to term this "homocamphene" α-methylfenchene, being homologous to α-fenchene. The same holds good for Wallach's "homofenchene", to which the term methylcamphene should be applied.

For obtaining the mixture of methylcamphene and methyl-α-fenchene from camphor the mixture resulting from treating camphor with Grignard's reagent and containing camphor and methylborneol was heated with sodium hydrogen sulphate. The hydrocarbon obtained by this reaction was heated with sodium and showed the melting-point 37 to 41°. The hydrocarbon mixture resulting from fenchone melted at 40 to 43°, and, after mixing with the hydrocarbon from camphor, at about 40°.

On working up the products of ozonisation of the hydrocarbon mixture from camphor, no other bodies except camphor and fenchone could be found. Ozonisation of the hydrocarbon mixture from fenchone passed off similarly; thus in both cases the reaction the results were not clear. On oxidation, however, of the hydrocarbon mixture from methylborneol and methylfenchylalcohol with chlorochromic acid in carbon disulphide solution, the author obtained camphanic aldehyde, m. p. 127°; semicarbazone, m. p. 220°.



Methyl-α-fenchene. Camphanic aldehyde.

Ruzicka finally discusses the systematics of Wagner's rearrangement and the formation of tricyclene in this transposition. For details, we must refer to the original paper.

On account of this publication of Ruzicka, J. Bredt[2]) report on work done, from 1914 until 1918, in common with M. Savelsberg, F. Goblet, A. C. Heinemann, and H. Dussier.

Basing on an observation made by Klages, that an excess of methyl magnesium iodide effects abstraction of water, further heating of the product resulting from camphor and methyl magnesium iodide with an additional molecule of the last-named compound led directly to the hydrocarbon $C_{11}H_{18}$. In order to free this body entirely from camphor it is treated once more with methyl magnesium iodide in ethereal solution. Camphor and fenchone yield on reaction with methyl magnesium iodide the tertiary alcohols methylborneol (I) and methylfenchol (II), which both, on splitting off water, yield principally the identical hydrocarbon $C_{11}H_{18}$ (III). On preparing this hydrocarbon from fenchone the method used for treating camphor proved to be unsatisfactory; in this case, it was advantageous to isolate the methylfenchol first which on further heating with acetic anhydride in a sealed tube up to 110° yielded the hydrocarbon.

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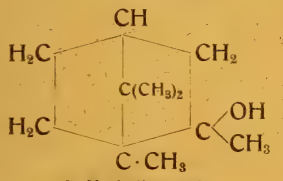
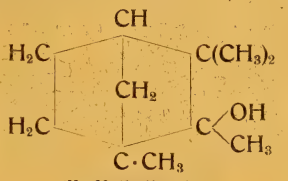
[1]) *Liebig's Annalen* **353** (1907), 210, 224; *Report* October **1907**, 140, 141. — [2]) *Journ. f. prakt. Chem.* II. **98** (1918), 96.

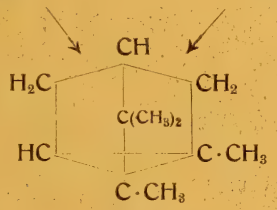
The hydrocarbon obtained from camphor as well as from fenchone boiled at 172 to 175°; m. p. 71 to 73°. On hydration by means of glacial acetic and sulphuric acids, both hydrocarbons yielded the identical acetates which on saponification gave the same alcohols and, on subsequent oxidation, the identical ketones and dicarboxylic acids. As to the constitution of the hydrocarbon, the oxidation with potassium permanganate offered a clue, since it revealed that the hydrocarbon was very stable towards that reagent. Evidently, the hydrocarbon has the constitution of a "homocyclene". This formula explains best the fact that, on hydration by means of glacial acetic and sulphuric acids, an acetate $C_{13}H_{22}O_2$ is obtained with the boiling point of *iso*-borneol; the acetate giving on saponification a secondary alcohol $C_{11}H_{20}O$, m. p. 193° (phenylurethane, m. p. 102°) which in turn gave, on oxidation, a ketone $C_{11}H_{18}O$ (m. p. 167 to 168°; oxime, m. p. 125 to 127°) yielding an acid $C_{11}H_{18}O_4$, m. p. 191° (anhydride, m. p. 205 to 207°). All of these products might be derivatives either of camphor or



(I) Methylborneol.



(II) Methylfenchol.



(III) Homocyclene.

of *iso*fenchone; many of their properties, *e. g.*, smell, crystallizing form, easy formation of the anhydrous acid, etc., however, point to their relation to the camphor series, which was furthermore proved by the measurement of the molecular refraction of the diethyl ester of the acid $C_{11}H_{18}O_4$. In this degradation, the hydrocarbon $C_{11}H_{18}$ behaved like its lower homologue, cyclene which, on hydration with glacial acetic acid and sulphuric acid, yields quantitatively *iso*bornylacetate[1]). The diethylester of the acid $C_{11}H_{18}O_4$ shows $d\frac{18.2°}{4°}$ 1.0289; the new acid is a 2-methylcamphoric acid; the ketone $C_{11}H_{16}O$ is termed by Bredt sec. β-methylcamphor.

When camphor is submitted to Grignard's reaction with phenylmagnesium bromide, phenylborneol results, which was obtained already by A. Haller and E. Bauer[2]), and which may be separated from unattacked camphor owing to its low volatility. On treating phenylborneol with acetic anhydride, a liquid hydrocarbon $C_{16}H_{20}$ is the result; $d\frac{14°}{14°}$ 0.9920; $[\alpha]_D$ + 3.27°. When brought in reaction with glacial acetic and sulphuric acids, an acetate is formed (m. p. 87°; b. p. 136° at 2 mm.), in addition to a hydrocarbon apparently isomeric with the original one; $d\frac{12.7°}{4°}$ 1.0034; $[\alpha]_D$ — 3.75°; b. p. 86° (2 mm.). The hydrocarbon yielding the acetate does not add hydrogen chloride; the one boiling at 86° (2 mm.) forms a hydrochloride, m. p. 76.5°, from which on treatment with milk of lime a tertiary alcohol, isomeric with phenylborneol, is obtained; b. p. 106.5° (2 mm.?); $[\alpha]_{D140°}$ (14°?) + 23.06°.

[1]) Compare, for instance, *Report* October **1905**, 100. — [2]) *Compt. rend.* **142** (1906), 77; *Report* October **1906**, 120.

On saponifying the acetate $C_{18}H_{24}O_2$, a secondary alcohol $C_{16}H_{22}O$, m. p. 115 to 116°, results, from which, by oxidation, a phenylcamphor, m. p. 68°, is obtained. By reduction of this ketone by means of sodium and alcohol, a mixture of phenylborneol and phenyl*iso*borneol is formed.

From phenylcamphor, phenylcamphoric acid is formed by the following process: — Sodio-potassium amide and amyl nitrite transforms phenylcamphor into the *iso*nitroso compound, m. p. 89°, from which, by treatment with sodium hydrogen sulphite, phenylcamphor quinone, m. p. 145°, is obtained. Prolonged treatment with potassium permanganate leads to the formation of phenylcamphoric acid m. p. 123.5°, which on dry distillation, or on treatment with acetyl chloride, yields the anhydride, m. p. 173.5°.

The α-naphthylborneol (resulting from camphor and α-naphthylmagnesium bromide) is equally very difficultly volatile with steam and may thus be separated from camphor; m. p. 122 to 124°. The abstraction of water from naphthylborneol is effected by dry distillation; the resulting hydrocarbon $C_{20}H_{22}$ melts at 92 to 93° and boils, under 16 mm., at 210°. On trying to prepare from this naphthylcamphene the sec.-naphthyl*iso*bornyl acetate, there was always formed an isomeric hydrocarbon $C_{20}H_{22}$, m. p. 116 to 117°.

On p. 114 of our *Report* October **1918** we dealt with a paper of H. Prins[1]) concerning exclusively open-chain unsaturated systems. Prins[2]) has now published new work on the same subject, entitled, Mutual condensation of unsaturated compounds in relation to terpenes, resins, and caoutchouc.

Amongst these condensations, these between $>C=C<$ and $>C=C<$ systems attract foremost interest.

In accord with the theory of the reciprocal activation the following bodies are expected to act as catalysts: — 1. bodies with the tendency to unite with the grouping C = C; 2. all the bodies actually uniting with the grouping C = C, independent of the stability of the compound formed, supposed that the experimental conditions are so chosen that the velocity of the reaction between the catalyst and the grouping C = C is small compared with the velocity of the mutual reaction of both the activated groups C = C. This depends of the nature of the substances and other conditions and will naturally be realised best if the interacting C = C groups are situated within the same molecule and if their mutual distance in the molecule is favourable for reaction.

A great number of compounds and elements belong to these two groups of catalysts, the "catalysts proper" and the "ephemeric catalysts": — acids, acid anhydrides, halogens and their compounds containing active halogen, sulphur and oxygen compounds with active sulphur or oxygen atoms. At higher temperature, the metallic oxides must be counted amongst them, which act as catalysts by their content either of active oxygen or of active metallic principles, finally the metals themselves owing to their tendency to form carbides.

Sulphur shows no particularly strong polymerising action; *e. g.*, pinene may be boiled for several days with sulphur without effecting considerable polymerisation.

In connection with his theoretical explanations, Prins deals with the formation of resin, the polymerisation of isoprene and of β-myrcene and with the vulcanisation of caoutchouc. For details, we refer to the original paper.

In a publication on the genetic correlation of the terpenes, O. Aschan[3]) gives a review of the terpene chemistry in concise form.

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[1]) *Chem. Weekblad* **14** (1917), 923; *Chem. Zentralbl.* **1918**, I. 168. — [2]) *Chem. Weekblad* **16** (1919), 64. — [3]) *Finska Kemistsamfundets* Jubilee Number, **1918**; *Chem. Zentralbl.* **1919**, I. 285.

Hydrocarbons.

Iso*pentane and isoprene.* — A publication by O. Aschan[1]) on derivatives of the petroleum pentanes and some of their homologues, deals, amongst others, also with isoprene and amyl alcohol. The author investigated the action of chlorine on paraffins, more especially the pentanes boiling from 30 to 38°, moreover a hexane, and the first runnings of the pentanes, b. p. 10 to 12°. Aschan succeeded, when starting from *iso*pentane, to synthesise the principal constituents of fusel oil, *i. e.*, both primary *iso*amyl alcohols (*iso*butyl carbinol and sec. butyl carbinol). The method devised permits of preparing these bodies cheaply and in unlimited quantities, as *iso*pentane occurs in all hitherto known petroleum varieties in considerable amount.

Furthermore, he endeavoured to make use of the *iso*pentane or of other suitable petroleum hydrocarbons (such as n-butane, n-pentane, various hexanes, more especially *n*-di*iso*propyl) for the preparation of isoprene and its homologues. He proved that all *iso*pentyl chlorides, by suitable elimination of hydrogen chloride, pass over into trimethylethylene, some of the chlorides thus suffering a rearrangement. Under certain conditions, trimethylethylene unites with chlorine, forming the corresponding dichloride, from which bases abstract hydrogen chloride with formation of isoprene. Equally, the dichloro*iso*pentanes obtained by direct chlorination of *iso*pentane (amongst which trimethylethylene chloride seems to be present) yield isoprene when sufficient heat is applied in eliminating the hydrogen chloride.

On studying the literature, Aschan found that the former investigators never had in hand the derivatives of *iso*pentane, but those of n-pentane.

In addition, Aschan communicates his observations on the distillation of caoutchouc and on derivatives of an isoprene obtained by heating vapours of turpentine oil. When distilling rubber he obtained, in addition to only 1,9 per cent. crude isoprene, 13 per cent. of a hydrocarbon (terpene?) hitherto not further investigated; b. p. 170 to 175°.

On pyrogenetic decomposition of the vapours of turpentine oil, about 5 per cent. of crude isoprene, b. p. 30 to 40°, resulted; in the last runnings, b. p. not exceeding 100°, at least two more hydrocarbons were present, amongst them particularly abundant a hydrocarbon unstable towards potassium permanganate, hence unsaturated; b. p. about 70°. The higher-boiling fractions contained, besides undecomposed terpenes, benzene and the next homologues thereof.

Finally, Aschan reports on new high-molecular hydrocarbons derived from isoprene. Under suitable conditions isoprene combines with unsaturated hydrocarbons, such as amylene, pinene, camphene, as well as with itself, forming very high-molecular compounds. They are amorphous, but lack entirely the physical properties of caoutchouc. Isoprene condenses likewise with *iso*pinene, dipentene, and sylvestrene.

In connection with the investigation mentioned before we report on a paper published likewise by O. Aschan[2]), *on the pyrogenic decomposition of the residues of Russian petroleum (masut); new suggestions for the economic utilisation of petroleum.* In this publication, the author is of opinion that the residue obtained in refining petroleum, commonly termed "masut", is a suitable raw material for the preparation of isoprene. He succeeded in obtaining isoprene amongst the distillation products of masut, and in converting it into caoutchouc, as well as in determining the amount of isoprene and the other hydro-

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[1]) *Öfversigt af Finska Vetenskaps-Societetens Förhandlingar* 58 (1915); *Chem. Zentralbl.* **1918**, II. 939, 955. — [2]) *Öfversigt af Finska Vetenskaps-Societetens Förhandlingar.* Helsingsfors 1919.

carbons of economic value which accompany the former, *i.e.*, benzene and toluene. The best method for preparing isoprene is that of destructive distillation by heat, such as employed in making oil gas on the large scale.

For the detection of isoprene, Aschan recommends a reaction published by him some time ago[1]). A small amount of the isoprene fraction is treated, in a test tube, with a little powdered anhydrous aluminium chloride, with ice-cooling, when very soon a gelatine-like yellowish precipitate is formed with simultaneous boiling-up. If the chilling is omitted, the sample gelatinises shortly, with spontaneous heating and formation of the condensation-product described by Aschan some time ago[2]), the ether-soluble modification equally being formed in considerable amounts. It must be taken into consideration that neither from pure isoprene nor from pure trimethylethylene the high-molecular hydrocarbons are obtainable. Neither does isoprene react in this manner when in mixture with pentane or *iso*pentane.

In addition to the aluminium chloride reaction, isoprene may be detected easiest, when in mixture with trimethylethylene, by means of the dichlorohydrin $C_5H_8Cl_2(OH)_2$[3]). The hypochlorous acid requied was prepared from sodium hypochlorite and boric acid. In a flask with a narrow neck, the sodium hypochlorite solution is cooled down to —5° and crystallised boric acid is added, then, drop by drop, 10 g. of the hydrocarbon, with shaking which is continued for one hour, and then the mixture is put aside for the night. After filtering, the liquid is saturated with salt, extracted with ether and the latter, after drying with sodium sulphate, evaporated, when a mixture of mono- and dichlorohydrins remains back. Purest isoprene dichlorohydrin melts at 81°.

Furthermore, isoprene may be detected by converting it into caoutchouc, a reaction which Aschan describes in detail.

Heptane. — That sometimes a mere chance leads to the detection of hitherto unknown reactions is proved by a short publication by E. V. Lynn[4]) dealing with a new reaction of the paraffines. During the course of some experiments with nitrosyl chloride, the author had prepared a saturated solution of this reagent in *n*-heptane — known to be the principal constituent of the turpentine oil from *Pinus Jeffreyi* — and accidentally set it in the sunlight for a day. When next observed the reddish-brown colour had changed to blue, and there was a precipitate of ammonium chloride. In a short time, the blue colour also disappeared and at the same time a heavy oil precipitated.

On examination on a larger scale, the saturated solution of nitrosyl chloride in heptane was preserved in the dark for weeks, without any apparent change in the reddish-brown colour. In the sunlight, however, the colour gradually changed to blue with a simultaneous precipitation of ammonium chloride. The blue colour quickly disappeared and the resulting turbid liquid gradually deposited a yellow oil, which evolved hydrogen chloride and some nitric oxide. The heptane was separated, saturated with nitrosyl chloride again and the process repeated until 50 g. of heavy oil had been obtained.

When submitted to steam distillation, the heavy oil gave off large quantities of hydrogen chloride. The distilled oil weighed 30 g. and had an intensely fragrant odor, likewise the aqueous distillate which contained hydroxylamine.

The oil boiled from 98 to 160°, the principal fraction from 144 to 150°, and contained, as would appear, besides heptane, a mixture of the three corresponding

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[1]) *Öfversigt af Finska Vetenskaps-Soc. Förh.* **58** (1915) A, No. 1, p. 74. — [2]) *Ibidem* No. 2, p. 6. — [3]) *Ibidem* No. 1, p. 73. — [4]) *Journ. Americ. chem. Soc.* **41** (1919), 368.

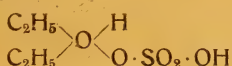
ketones: methylamyl ketone, ethylbutyl ketone, and dipropyl ketone, the latter predominating. Thid ketone, when prepared from calcium butyrate, yielded a semicarbazone of the m. p. 125°; the corresponding fraction from the heavy oil, however, gave no semicarbazone on treatment with semicarbazide. A further examination of this fraction will be necessary to identify it as dipropyl ketone.

C. E. Andrews[1]) reports on *the nitration of* p-*cymene to mononitrocymene*-1,2,4. The matter being only of minor importance for our branch of chemistry, we content ourselves with a short abstract. The yields of the methods described hitherto in the literature are very low. A yield of 85 per cent. is obtained by the following method: — One-half mol of *p*-cymene was added to an equal weight of sulphuric acid (d 1.84) with stirring, the temperature being kept constantly below 0°. A well-cooled mixture of 50 g. of nitric acid (d 1.42) and 105 g sulphuric acid (d 1.84) was then added drop by drop to the sulphuric acid solution of the hydrocarbon, keeping the temperature at 0° or below and stirring the mixture efficiently. After the acid mixture is added (in 5 hours) the reaction was allowed to proceed for from 15 to 30 min., the mixture then poured into cold water, the oily product washed well and distilled with steam or *in vacuo*; b. p. 115 to 116° (3 to 5 mm. pressure). It consisted in the main of comparatively pure mononitrocymene. Small amounts of *p*-toluic acid and of *p*-tolylmethylketone are produced as by-products, but no isomeric mononitrocymene. Reduction of the mononitrocymene by means of tin and hydrochloric acid resulted in the quantitative formation of the corresponding amine.

Concerning *the identification of* p-*cymene*, see p. 56 of the present *Report*.

On the *transformation of* p-*cymene from spruce turpentine spirits into carvacrol*, see p. 57 of this *Report*.

Reaction of terpenes with diethyl oxonium sulphate. — Amongst the oxonium compounds, O. Aschan[2]) counts the mixture of stœchiometrical amounts of absolute ether and sulphuric acid monohydrate, in which be presumes — evidently correctly — the existance of diethyloxonium sulphate: —



This mixture was allowed to act on several terpenes whereby alcohols as well as hydrocarbons were obtained. Apparently, it is here the case of hydration reactions which pass off with catalytic action of diethyloxonium sulphate.

The experiments proceeded best with camphene, by adding a little more than 1 molecule of sulphuric acid monohydrate, drop by drop, with strong cooling by means of ice and salt, to 1 molecule of absolute ether, then by adding, in three portions, about 10 per cent. less than the molecular quantity of camphene. After adding each portion the temperature of the mixture was allowed to rise slightly by removing the flask from the cooling mixture, but not above 20°; before adding the next portion of camphene, the mixture was cooled down again. After all the camphene was added, the mixture was allowed to stand some time at room temperature, then given drop by drop to a saturated solution of sodium carbonate in excess containing

[1]) *Journ. ind. eng. Chemistry* **10** (1918), 453. — [2]) *Meddelanden fran K. Vetenskapsakademiens Nobelinstitut* **5** (1919), No. 8.

some solid crystallised Na_2CO_3. From the solution obtained, the supernatant ether layer was drawn off and the aqueous layer extracted twice with sufficient ether, then distilled with steam, when *inter alia* inactive camphene hydrate[1]) was obtained. Aschan carried out some more experiments with camphene and diethyloxonium sulphate and experienced the best yields of camphene hydrate when equal mols of sulphuric acid and ether were employed. From the by-products be isolated a diterpene, b. p. 315°, formed probably by condensation. The yield of camphene hydrate seemed to be raised when water was added to the oxonium reagent.

Aschan tried next to errive at *iso*bornyl esters by aid of the reagent. For this purpose, the well-cooled oxonium mixture was first treated with camphene, then with formic acid; the principal product obtained was *iso*bornyl formiate.

Santene, on treatment with the oxonium reagent, gave a mixture of α- and β-santenol.

Dipentene, when acted upon in the same manner, gave rise mainly to a diterpene; terpineol likewise yielded almost exclusively polymerisation products.

α-Pinene formed terpenes, apparently dipentene; β-pinene gave a diterpene. It could not be ascertained whether in these reactions terpineol was formed as intermediate product.

Pinene. — As is well known, optically inactive or but poorly active α-pinene gives easily rise to a nitrosochloride, but not when strongly active[2]). E. V. Lynn[3]) explains this phenomenon in virtue of his experiments by the fact that the active α-pinene nitrosochloride is extremely soluble in the usual organic solvents. In his opinion, the acetic acid and the water present when preparing the nitrosochloride after Wallach's directions easily alter this active compound, making its isolation impossible, the method was modified by elimination of the acetic acid and by substituting alcoholic hydrogen chloride for the aqueous hydrochloric acid. He preperes α-pinene nitrosochloride as follows: — equal volumes of pinene, ethyl nitrite, and absolute alcohol are mixed and cooled in a freezing mixture. A solution of alcoholic hydrogen chloride is added, in amount corresponding to the theoretical requirements for the pinene used. The temperature is kept below — 5°. After standing about one-half hour the crystals are filtered off. In the preparation of larger quantities, the absolute alcohol may be replaced by alcohol of 95 per cent. The yield is slightly better than by Wallach's method.

The filtrates from the above preparation, after the further addition of one to two volumes of alcohol, were exposed to temperatures below — 10°. After some time, crystals separated in the form of colourless, transparent needles which were purified by washing with cold alcohol. The best yield, as was expected, was obtained from α-pinene of high rotation from the wood oil of *Chamæcyparis Lawsoniana*, (Murr.) Parl.[4]), $[\alpha] + 47.7°$, which gave no trace of inactive, but about 15 per cent. yield of the active nitrosochloride. This new compound had the m. p. 81 to 81.5° and a rotation, in alcohol or chloroform solution, of about 322°, the direction being the same as that of the pinene employed.

The active nitrosochloride of α-pinene is insoluble in water, but dissolves, at 20°, in 200 parts of alcohol or 50 parts of heptane, and is very soluble in pinene, chloroform, ether, acetone, ethyl acetate, pyridine, ethyl nitrite, benzene, and fatty oils, but less so in methyl or amyl alcohol. The solution in heptane or chloroform is blue at

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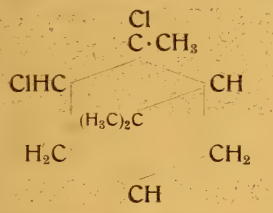
[1]) Comp. *Report* October **1911**, 132. — [2]) Comp. *Report* April **1910**, 164. — [3]) *Journ. Americ. chem. Soc.* **41** (1919), 361. — [4]) A. W. Schorger, *Journ. ind. eng. Chemistry* **6** (1914), 631; *Report* April **1915**, 12.

or above room temperature, but becomes colourless at 0°. The crystals are more unstable than the inactive product. They react readily with benzylamine, piperidine, with alcoholic alkali to form nitrosopinene, and with aniline. The benzylamine derivative melts at 144 to 145°; $[\alpha]_D$ about 92° in 2.5 per cent. acetone solution. The piperidide melts at 84°; $[\alpha]_D$ about 50°.

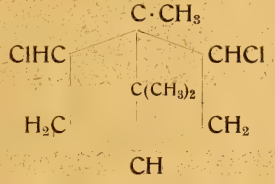
The active nitrosochloride readily reacts with aniline to form active pinene: — b. p. 155 to 159°, $[\alpha]_D$ about 53.75° (in 4 per cent. alcoholic solution), n_D 1.470. The maximum rotation observed with natural α-pinene is, according to Lynn, + 51.52°[1]). d-α-Pinene yielded an inactive hydrochloride, m. p. 118°.

The poor yields of pinene nitrosochloride (about 50 per cent.) are, according to Schorger, due not alone to the formation of readily soluble active nitrosochloride, but also to side reactions. The disappearance of the blue colour and the precipitation of crystals is accompanied by an evolution of gas which, by the usual reagents, proved to be nitrogen. Lynn was unsuccessful in trying to obtain well-defined bodies from the mother liquors of the preparation of the nitrosochloride.

Two publications by Aschan[2]) on *the chlorination of pinene* and the additive power of unsaturated compounds show that little was hitherto known about the former subject. He investigated the action of chlorine in carefully dried solvents at temperatures between — 15° and zero. The results were in no accord with the earlier statements. The action of the halogen passed off in a complex way. The first fractions of the product yielded abundant quantities of solid pinene hydrochloride. From the higher fractions, the only body which could be isolated was a pinene dichloride (II) (?), which is possibly formed by rearrangement of a primarily-formed normal dichloro addition product (I). It presented itself in shape of water-white, rhombic bi-pyramidic tabular



(I) Normal dichloro addition product of α-pinene.



Pinene dichloride formed by rearrangement of (I).

crystals, m. p. 173 to 174°; b. p. about 130° (10 mm.). In addition, a liquid dichloride appeared to be formed; b. p. 120 to 125° (10 mm.) which, however, could not be obtained in the pure state. Both chlorides were not attacked by boiling with aniline.

Preliminary experiments showed that on further chlorination of pinene hydrochloride in chloroform or carbon tetrachloride up to four hydrogen atoms may readily be substituted by chlorine yielding white crystalline products of the m. p. 135°, 150 to 152°, and 130°. The analytical data lay between $C_{10}H_{15}Cl_3$ and $C_{10}H_{14}Cl_4$; a dichloride could not be isolated.

Further experiments of Aschan demonstrated that the action of pinene on various terpene hydrochlorides, especially at higher temperature, regularly passes off in this manner that hydrogen chloride is split off from the hydrochlorides with formation of ordinary pinene hydrochloride (bornyl chloride). This reaction was observed in the

[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. I. p. 293. — [2]) *Öfversigt af Finska Vetenskaps-Societetens Förhandlingar* **57** (May 4, 1915); **58** (Dec. 20, 1915); *Chem. Zentralbl.* **1918**, II. 952, 953.

case of the dihydrochlorides of dipentene, sylvestrene, and camphene and the monohydrochlorides of dipentene. Pinene abstracts hydrogen chloride slowly from aniline hydrochloride and even from sal ammoniac. Nopinene and the new bicyclic terpene prepared recently[1]) from Finnish oil of turpentine (provisionally termed *γ*-pinene) behave like pinene. Aschan found that likewise camphene hydrobromide and dipentene dihydrobromide are decomposed by pinene, with abstraction of hydrogen bromide, and that pinene, when heated with aniline sulphate in glacial acetic acid solution, yields *iso*bornyl acetate, evidently acting hereby as a base owing to its unsaturated character. Even from such complex halogen addition products such as dipentene tetrabromide, pinene abstracts hydrogen halide.

Aschan believes this capacity of pinene and allied terpenes of abstracting hydrohalogen to be due to the comparatively great quantity of latent heat in these terpenes.

Camphene. — Some years ago, we reported on a paper by D. E. Tsakalotos and B. Papaconstantinou[2]), in which the authors described a method of preparing highly-rotatory *d*-camphene ($[\alpha]_D$ + 84.05°, 10 per cent. solution in benzene) by heating *d*-pinene hydrochloride with sodium phenate. The authors have now[3]) transformed this camphene into l-*iso*bornyl acetate by means of glacial acetic + sulphuric acid or glacial acetic acid + zinc chloride and measured the change in the rotation compared with the time. The *iso*bornyl acetate thus obtained showed d_{150} 0.991, $[\alpha]_D$ — 3.93° (in substance). Camphene in solution with glacial acetic acid without sulphuric acid or zinc chloride shows no change in the optical rotation even after two days. In an experiment with glacial acetic + sulphuric acids, a mixture of 10 g. *d*-camphene, 25 g. glacial acetic acid, and three drops of about 50 per cent. sulphuric acid was observed in a 10 cm. tube at 21 to 24°. The rotation was: —

α_D + 21.13°	after 3 minutes	α_D + 1.85°	after 1022 minutes
α_D + 20.55°	„ 9½ „	α_D + 0.20°	„ 1232 „
α_D + 19.86°	„ 22 „	α_D ± 0	„ 1257 „
α_D + 18.83°	„ 47 „	α_D — 1.30°	„ 1472 „
α_D + 16.38°	„ 107 „	α_D — 5.54°	„ 3842 „
α_D + 15.33°	„ 137 „	α_D — 5.88°	„ 7650 „
α_D + 14.15°	„ 197 „		

In one of the experiments with glacial acetic acid and zinc chloride, the rotation was constant, after 10000 minutes, at — 2.62°.

The *iso*borneol obtained from *iso*bornyl acetate on treatment with potassium hydroxide was optically inactive and gave, on oxidation, *i*-camphor, m. p. 172°.

Fenchene. — Some time ago, G. Komppa and R. H. Roschier[4]) reported on a total synthesis of *α*-fenchene, thereby confirming the formula for fenchene established by Wallach.

An extensive paper appeared later on from the pen of W. Qvist[5]), from which we gather some welcome contributions to our knowledge on the rather complicated chemistry of fenchene. Some reactions described by him have been published before in abridged form[6]).

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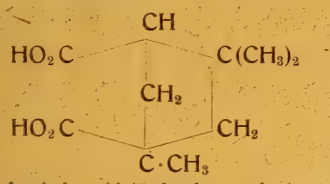
[1]) *Teknikern* **25**, 31; comp. *Report* October **1916**, 58. — [2]) *Journ. de Pharm. et Chim.* VII. **14** (1916), 97; *Report* October **1917**, 147. — [3]) *Ibidem* VII. **17** (1918), 198. — [4]) *Chem. Zentralbl.* **1917**, I. 751; *Report* October **1917**, 144. — [5]) *Liebig's Annalen* **417** (1918), 278. — [6]) Comp. *Chem. Ztg.* **41** (1917), 347; *Report* October **1917**, 146.

Before entering into the details of Qvist's work, we wish to state that the terms α- and β-fenchene were used by Komppa and Roschier[1]). They termed Wallach's *D, l*-fenchene, "*l*, α-fenchene" and his *D, d*-fenchene, "*d*, β-fenchene", and the racemic form of this hydrocarbon, "*d, l*-β-fenchene". Although Wallach's terms have hitherto been universally used in the literature, they give rise to difficulties when it is the case of inactive fenchenes, and this was the reason why Komppa and Roschier suggested the new names.

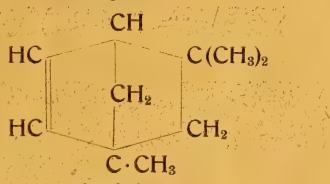
Firstly, Qvist reports on fenchenes prepared from fenchyl alcohol which was obtained from *D*-fenchene by reduction. Wallach's method — reduction with sodium in ethyl alcoholic solution — did not give the good yield as did the process of Gardner and Cockburn[2]) (sodium and amyl alcohol). In order to obtain a quite pure preparation, Qvist transformed the alcohol into its oxalate (m. p. 92.5 to 93.5°) by heating it for 5 hours to 125° with oxalic acid; on saponification of the oxalate, the pure *D, l*-fenchyl alcohol resulted. M. p. 46.5 to 47°; b. p. 201 to 202°; $[\alpha]_D$ — 12.93°. In the same manner, *L, d*-fenchyl alcohol was obtained from the oxalate (m. p. 92 to 93°). From the racemic mixture of the oxalates, Qvist prepared, by saponification racemic fenchyl alcohol; m. p. 35.5 to 37°; b. p. 200 to 201° (755 mm.).

Direct abstraction of water from fenchyl alcohol was most readily effected by heating with aluminium phosphate or potassium hydrogen sulphate; the latter yielding additionally more lower-boiling hydrocarbons than the former.

From *D, l*-fenchyl alcohol, Qvist obtained, by heating with $KHSO_4$ in a metallic bath up to 200°, a mixture of hydrocarbons boiling between 139 and 157° (759 mm.). A fraction boiling from 141 to 143°, contained *l*, α-fenchene, which was proved, *inter alia*, by oxidation to *l*-hydroxy-α-fenchenic acid[3]). Likewise, *iso*fenchylene was present in this fraction, on oxidation with potassium permanganate that hydrocarbon yielded *cis-d, l-iso*fenchoic acid[4]) (*iso*fenchocamphoric acid). The constitution of this acid being known, the following structural formula applies to *iso*fenchylene: —



*d, l-Iso*fenchoic acid (*Iso*fenchocamphoric acid).



*Iso*fenchylene.

*Iso*fenchylene is identical with the fenchylene of Nametkin and Rushenceva[5]) obtained by the xanthate method. Equally, the hydrocarbon prepared by Komppa and Roschier[6]) and termed by them δ-fenchene or *iso*fenchene, is identical with *iso*-fenchylene. Qvist adopts this name since it reveals the relation of the hydrocarbon to *iso*fenchyl alcohol, as with bornylene and borneol.

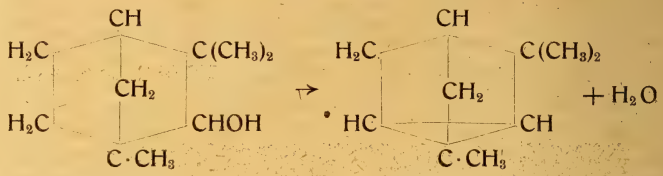
The fraction of b. p. 152 to 155° contained *d*, β-fenchene and yielded on oxidation with $KMnO_4$ *d*-hydroxy-β-fenchenic acid (*D, d*-hydroxyfenchenic acid). The parts not attacked by $KMnO_4$ contained *cyclo*fenchene, b. p. 141.5 to 142° (755 mm.).

Qvist prepared furthermore fenchenes from fenchyl alcohol by the xanthate method, a process formerly made use of by us and by Tchugaeff[7]), however, with less favourable

[1]) *Annal. Acad. Scient. Fenn., Ser.* A 7 (1916), No. 14; *Chem. Zentralbl.* **1917**, I. 407. — [2]) *Journ. chem. Soc.* **73** (1898), 276. — [3]) Comp. Wallach, *Liebig's Annalen* **362** (1908), 184; *Report* November **1908**, 190. — [4]) Comp. Aschan, *Liebig's Annalen* **387** (1912), 51; *Report* April **1908**, 179. — Sandelin, *Liebig's Annalen* **396** (1913), 315; *Report* October **1913**, 149. — [5]) *Journ. Russ. phys.-chem. Soc.* **48** (1916), 450; *Report* October **1917**, 146. — [6]) *Annal. Acad. Scient. Fenn., Ser.* A, 8 (1917), No. 15, p. 5; *Report* October **1918**, 117. — [7]) *Chem. Ztg.* **23** (1899), 1061; *Report* April **1900**, 54.

results. The fenchyl xanthate obtained by Qvist was a light yellow, feebly-smelling oil, b. p. 162° (18 mm.). The ester was decomposed in quantities of 30 to 40 g. by heating up to about 230°. 223 g. of the xanthate yielded 90 g. hydrocarbon (= 72.4 per cent.); the mixture boiled from 139° to 157.5°. From the fraction b. p. 139 to 142.5° Qvist prepared quite pure *d-cyclo*fenchene by shaking it repeatedly, at 55°, with a solution of $KMnO_4$. After distilling over sodium *d-cyclo*fenchene boiled from 140.6 to 141.4°; $d_{4^\circ}^{20^\circ}$ 0.8586; $[\alpha]_D$ + 0.77°; $n_{D19.3^\circ}$ 1.45202. Except the direction of the rotation, the hydrocarbon is identical with Aschan's *β*-pinolene[1]) (see below). It added bromine with formation of *d*, *α*-fenchene dibromide (m. p. 86 to 87°); on hydration according to Bertram and Walbaum it yielded *l-iso*fenchyl alcohol.

The formation of *cyclo*fenchene from fenchyl alcohol passes off in the following manner: —



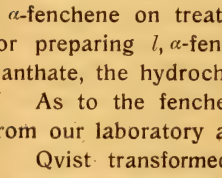
On adding hydrogen chloride to *d-cyclo*fenchene and abstracting HCl from the hydrochloride by means of *o*-toluidine, either no *cyclo*fenchene, or at least an only very small amount, is regenerated, but *l*, *α*-fenchene instead. With ethyl nitrite and hydrochloric acid, *cyclo*fenchene gives no reaction.

The higher fractions of the mixture of hydrocarbons from the xanthate contained *l*, *α*-fenchene.

Since *d-cyclo*fenchene and *l*, *α*-fenchene yield the same hydrochloride which forms *l*, *α*-fenchene on treatment with *o*-toluidine, this reaction offers a very ready method for preparing *l*, *α*-fenchene. It is not necessary to purify the fenchene from the xanthate, the hydrochloride being prepared directly from the crude product.

As to the fenchenes derived from *iso*fenchyl alcohol, work has been published from our laboratory already years ago[2]).

Qvist transformed *iso*fenchyl alcohol into its chloride by means of PCl_5 and decomposed it with *o*-toluidine, whereby very pure *d*, *β*-fenchene resulted. *l-Iso*fenchyl alcohol was purified, *inter alia*, by its acid phthalate, when, in addition, the neutral phthalate was formed; m. p. 110 to 110.5°.



d, *β*-Fenchene, after distilling over sodium, boiled from 150 to 153°. Oxidation with $KMnO_4$ gave rise to *d*-hydroxy-*β*-fenchenic acid, m. p. 137 to 138°. With bromine, *d*, *β*-fenchene passed over into a new, solid dibromide (m. p. 81 to 82°) which was not identical with *l*, *α*-fenchene dibromide. Furthermore, it yielded a solid nitrosochloride which, however, showed no constant melting point. This formation of a solid nitrosochloride from *d*, *β*-fenchene is in contradiction to Meyer's[3]) statement that hydrocarbons with the double linkings in the positions $>CH:CH_2$ — $CH:CH$ — and — $CH:CH_2$ yield

[1]) *Liebig's Annalen* **387** (1912), 34; *Report* April **1912**, 188. — [2]) Bertram and Helle, *Journ. f. prakt. Chem.* II. **61** (1900), 303; *Report* April **1900**, 56. — [3]) *Analyse und Konstitutionsbestimmung organischer Verbindungen*, 2nd ed., Berlin 1909, p. 939.

no solid nitrosochlorides; Weyl[1]) states that solid nitrosochlorides are formed principally from the grouping $R_2C:CHR$. *Iso*fenchylene is likewise an exception from these rules.

Qvist obtained this hydrocarbon from *iso*fenchyl xanthate which even *in vacuo* could not be distilled without decomposition. The *iso*fenchylene from the xanthate boiled from 138.5 to 141° and manifested the properties described by Kondakov and Lutchinine[2]). On oxidation with $KMnO_4$ is yielded *cis-l-iso*fenchoic acid, m. p. 157 to 157.5°; with bromine and with hydrogen chloride, only oily products were obtained, whereas the nitrosochloride and the nitrosate were solid bodies; the former melted at 142°, the latter unsharply.

On comparing the *cyclo*fenchene prepared by Qvist with an original preparation of Aschan[3]) of β-pinolene from pinene hydrochloride the former proved to be a feebly dextrorotatory *d-cyclo*fenchene, the latter a mixture of *l*- and *d, l-cyclo*fenchene. Aschan's hydrocarbon, namely, yielded on bromination two solid dibromides, of which one was identical with *l*, α-fenchene dibromide, the other with *d, l*-fenchene dibromide. Aschan's preparation actually showed a distinct, although very weak lævorotation:— $[\alpha]_{D18°} -0.28°$.

Finally, Qvist studied the behaviour of the solid dibromide (m. p. 87 to 88°) resulting from *cyclo*fenchene as well as from α-fenchene. On treatment with zinc and alcohol, *d*. α-fenchene dibromide yielded *l*, α-fenchene and fenchane. This result, however, allowed not of drawing any positive conclusions as to the constitution of α-fenchene dibromide.

R. H. Roschier[4]), in a lengthy paper, reports on the *ozonisation of apobornylene and of the various fenchenes*. This work is a continuation of the investigations of Komppa and Hintikka[5]) on the same subject. It was now proved that the hydrocarbon hitherto termed apobornylene is a mixture of two isomeric hydrocarbons, of which one is real apobornylene (I), the other being tricyclic apocyclene (II). Furthermore, Roschier found the fenchene hydrocarbon to consist of a mixture of at least five terpenes, two of which are semicyclic, two endocyclic, and one tricyclic. As was proved by ozonisation, the formula proposed for *d*-fenchene[6]) — identical with Wallach's *D, l*-fenchene — was fully confirmed. The second semicyclic, β-fenchene, being identical with Wallach's *D, d*-fenchene, is constituted as per formula IV. The hydrocarbon of the b. p. 145 to 147° has, in its main part, the double linking in the cycle, as is showed by formula V. The lowest-boiling fenchene possesses for certain the formula VI suggested by Semmler for iso*allo*fenchene. In the low-boiling fractions of fenchene, a small amount of *cyclo*-fenchene, identical with Aschan's β-pinolene, is found.

The apobornylene used in Roschier's experiments was prepared in one case from camphenilol by means of Tchugaeff's xanthate method, in another case from camphenilone and its dichloride. The hydrocarbon obtained from camphenilol methyl xanthate was a tough, camphoraceous body, m. p. 38°, b. p. 138° (760 mm.). The product from camphenilone remained oily at ordinary temperature and congealed only after slight cooling. On dry distillation of camphenilylamine phosphate, in a CO_2-current, according to Harries, there was formed camphenilylamine, and not the hydrocarbon expected.

When ozonised, apobornylene yielded a solid ozonide $C_9H_{14}O_3$ of normal composition which was fairly stable at ordinary temperature and which was split up, in glacial acetic acid solution, chiefly into three fractions of which the one of the lowest boiling point was an oil with an ester-like smell. The medium fraction had aldehydic

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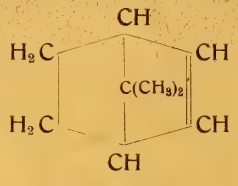
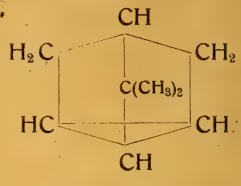
[1]) *Die Methoden der organischen Chemie.* Leipzig 1911, vol. II, p. 639. — [2]) *Chem. Ztg.* **25** (1901), 131; *Journ. f. prakt. Chem.* II. **75** (1907), 540; *Reports* April **1901**, 64; October **1907**, 148. — [3]) *Liebig's Annalen* **387** (1912), 49; *Report* April **1912**, 188. — [4]) *Annal. Acad. Scient. Fenn., Ser.* A. **10** (1919), N° 1, p. 1; *Chem. Zentralbl.* **1919**, I. 726. — [5]) *Liebig's Annalen* **387** (1912), 296; *Berl. Berichte* **47** (1914), 512; *Reports* April **1912**, 187; April **1915**, 95; October **1918**, 117. — [6]) Misprint, in lieu of α-fenchene?

properties, but was not uniform and contained peroxides. From the highest-boiling fraction, crystallised apocamphoric acid anhydride (m. p. 174 to 175°) was isolated. 20 to 30 per cent. of the hydrocarbon employed remained unattacked on ozonisation and contained a new hydrocarbon C_9H_{14} which was very volatile and tough, particularly stable towards $KMnO_4$, and showed a sweet and at the same time biting smell resembling camphor. Roschier termed this hydrocarbon apo*cyclene*. Owing to its molecular refraction, it must be regarded as of tricyclic constitution represented by formula II. M. p. 42.5 to 43°; b. p. 138 to 139° (760 mm.); $d_{4^\circ}^{40^\circ}$ 0.8710; n_{D40° 1.45144.

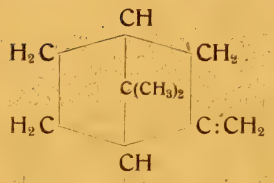
When ozonising the apobornylene prepared according to Tchugaeff, the major part of the hydrocarbon remained unattacked; 62 per cent. thereof were apocyclene.



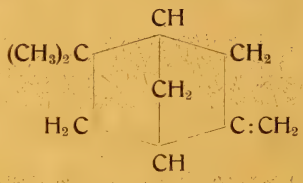
(I) Apobornylene.



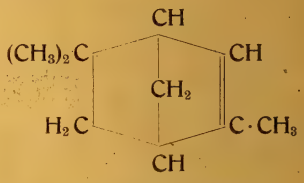
(II) Apocyclene.



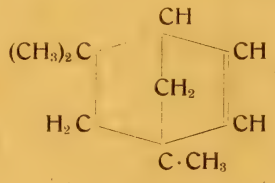
(III) *d*-Fenchene[3]).



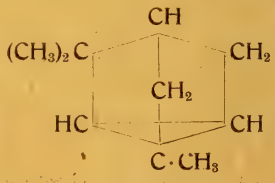
(IV) *β*-Fenchene.



(V) Fenchene hydrocarbon, b. p. 145 to 147°.



(VI) Iso*allo*fenchene.



(VII) *Cyclo*fenchene (*β*-pinolene).

On treatment with glacial acetic + sulphuric acids, apocyclene formed an acetate $C_{11}H_{18}O_2$ which had also been found amongst the scission-products of apobornylene ozonide. B. p. 81 to 82° at 8 mm.; $d_{4^\circ}^{20^\circ}$ 0.9971; n_{D20° 1.4623. The alcohol of this acetate yielded, on oxidation, first *β*-fenchocamphorone (m. p. 60 to 63°; semicarbazone, m. p. 200 to 201°), and subsequently *trans*-apofenchocamphoric acid, thus revealing itself as *β*-fenchocamphorol.

The sample of *α*-fenchene examined by Roschier was prepared from fenchyl chloride according to Wallach; b. p. 155 to 160°; $d_{4^\circ}^{17.5^\circ}$ 0.8670; α_D — 32.32°; $n_{D17.5^\circ}$ 1.46729. The ozonide of this hydrocarbon was a viscous, colourless oil which did not explode on heating. The values resulting on combustion showed that *α*-fenchene had formed compounds with more oxygen than corresponds to a normal ozonide. On scission, the author obtained about 50 per cent. of *α*-fenchocamphorone (Wallach's *D, d*-fenchocamphorone) which Komppa and Hintikka had prepared by ozonisation of *α*-fenchene from fenchylamine; b. p. 198 to 200°; semicarbazone, m. p. 220 to 221°. In addition, there were formed a neutral oil of aldehyde-like behaviour, which, however, could not

be purified, and a saturated monocarboxylic acid which was already isolated by Komppa and Hintikka, but which was not further investigated by them. Roschier terms this acid *α*-fenchylanic acid; the only structure possible is that of dimethyl-7,7-bi*cyclo*-(1,2,2)-heptane-2-carboxylic acid; m. p. 71.5 to 72°; anilide, m. p. 149.5 to 150°.

The mixture of hydrocarbons used for the investigation of *β*-fenchene and its accompanying hydrocarbons was prepared by distilling *d, l*-fenchyl alcohol (m. p. 33 to 35°; b. p. 198°), in a current of CO_2, with potassium or sodium hydrogen sulphate. *β*-Fenchene is contained in the highest-boiling of the mixture (b. p. 151 to 153°). *β*-Fenchene ozonide is a viscous, syrupy oil containing likewise more oxygen than the normal ozonide. By scission, an impure *β*-fenchocamphorone was obtained; further oxidation gave some apocamphoric anhydride (from *α*-fenchocamphorone present) and in the main an acid obtained formerly by Komppa and Roschier by direct oxidation of *β*-fenchene. The acid was isomeric with apocamphoric acid and was dimethyl-4,4-*cyclo*pentane-1,3-dicarboxylic acid (Nametkin's and Chuchrikowa's[1]) apofenchocamphoric acid), m. p. 144 to 145°. Inasmuch as an anhydride was unobtainable, the acid seems to be the *trans*-isomeride.

The medium fraction of the hydrocarbon mixture, on ozonisation, proved to contain an endocyclic double-bond; it represents a mixture of two hydrocarbons, one of which is doubtless identical with iso*allo*fenchene (VI), the other being probably of the formula (V). Cleavage of the ozonide gave rise, in the main, to a dialdehyde and a ketonic acid. The dialdehyde $C_{10}H_{16}O_2$ resulting from iso*allo*fenchene, is a light yellow oil; b. p. 118 to 120° (10 mm.); $d^{20°}_{4°}$ 1.0215; $n_{D20°}$ 1.4700; disemicarbazone, m. p. 219°. The crude aldehyde fraction contained a small amount of *d, l-iso*fenchocamphoric acid. The ketonic acid $C_{10}H_{16}O_3$ is, in all probability, a derivative of the hydrocarbon (V); $d^{20°}_{4°}$ 1.0924; $n_{D20°}$ 1.4774; semicarbazone, m. p. 220 to 221°. The acid contained the grouping $-CO\cdot CH_3$, since on treatment with alkaline hyprobromite solution a dicarboxylic acid $C_9H_{14}O_4$ (m. p. 147 to 148°) was formed, with splitting-off of bromoform. This acid was not identical with the apofenchocamphoric acid obtained on oxidation of *β*-fenchocamphorone. Probably, it is here a case of the *cis*-isomeride of apofenchocamphoric acid.

From the degradation-products of the lowest-boiling fraction of the *β*-fenchene hydrocarbon mixture there was obtained, in addition to aldehydic and acid compounds, a small amount of a volatile, pleasantly smelling, oily ketone $C_9H_{14}O$ (semicarbazone, m. p. 209°) which on oxidation yielded a dibasic acid $C_9H_{14}O_4$. The acid fraction, contained, besides small amounts of the ketonic acid described above (semicarbazone, m. p. 220 to 221°), a fair amount of racemic cis-*iso*fenchocamphoric acid (m. p. 173 to 174°) and an aldehydic acid which on further oxidation passed over into the same *cis*-iso-fenchocamphoric acid, thus proving that the lowest-boiling fraction of the fenchene hydrocarbons consisted principally of iso*allo*fenchene (VI).

The part of this fraction remaining unattacked on treatment with ozone is a *cyclo*-fenchene and identical with Aschan's *β*-pinolene (VII); b. p. 142 to 143°; $d^{16.5°}_{4°}$ 0.8624; $n_{D16.5°}$ 1.45364; hydrochloride, m. p. 26 to 28°; hydrobromide, m. p. +4°, b. p. 92 to 93° (12 mm.). *Cyclo*fenchene was, like *β*-pinolene, transformed into the acetate of *iso*fenchyl-alcohol, then the free alcohol, *iso*fenchene and *d, l-iso*fenchocamphoric acid.

Some time ago A. C. Chapman[2]) described a new hydrocarbon "spinacene" occurring in the fatty oil obtained from the liver of certain *Spinacidæ* (fishes of the shark family),

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[1]) Comp. *Reports* October **1917**, 146; October **1918**, 133. — [2]) *Journ. chem. Soc.* **111** (1917), 56; **113** (1918), 458.

e. g., Centrophorus granulosus and *Scymnus lichia.* Originally, Chapman suggested the formula $C_{30}H_{50}$ for this hydrocarbon, later on, the formula $C_{29}H_{48}$. Strange to say, spinacene, on distillation with sodium gives, *inter alia,* rise to a hydrocarbon $C_{10}H_{18}$, which the author proved to be a *cyclo*dihydroterpene, in all probability *cyclo*linaloolene. After repeated distillation with sodium, the terpene boiled at 51 to 54° (10 mm.), or at 170 to 175° (ord. pressure) with slight polymerisation; $d_{15°}$ 0.8149, $n_{D20°}$ 1.4565. The hydrocarbon added two atoms of bromine. Its properties agreed well with the constants quoted in literature[1]) for *cyclo*linaloolene or *cyclo*dihydromyrcene.

The former hydrocarbon had been prepared formerly by Semmler by treating linaloolene, a reduction-product of linalool, with concentrated sulphuric acid. *Cyclo*dihydromyrcene was obtained by the same author by inversion of dihydromyrcene and described as an isomeride of *cyclo*linaloolene.

The result of Chapman's investigation is of high interest from the physiological point of view, since it reveals the connection of a hydrocarbon of animal origin with the terpenes which hitherto are known to be of exclusively vegetable origin.

Alcohols.

On the preparation of *heptyl alcohol from œnanthol,* see p. 71 of this *Report.*

In order to identify *the terpene alcohols or phenols* occurring frequently in essential oils, the phenylurethanes are often resorted to, for which purpose the alcohols or phenols are usually treated with the calculated amount of phenyl *iso*cyanate at room temperature or with slight heating, sometimes with addition of aluminium chloride. F. Weehuizen[2]) recommends a different process, consisting in heating the ingredients in a solution of a petroleum fraction of the b. p. 170 to 200°. The advantages offered by this solvent (consisting principally of decane and undecane) are said to be the following:— 1. Since there is no water present, formation of diphenylurea is impossible.— 2. The terpene alcohols and the phenols as well as phenyl*iso*cyanate are soluble in the petroleum fraction.— 3. The urethanes formed are difficultly soluble in the fraction and are precipitated therefrom, on cooling, in well-formed crystals.

Weehuizen dissolves 1 g. of the terpene alcohol or phenol in about 6 to 10 ccm. of the petroleum fraction, adds the necessary quantity of phenyl*iso*cyanate and boils the mixture for 30 to 60 minutes; sometimes, longer boiling is necessary. Some of the phenylurethanes are difficultly soluble even in the boiling solvent; in such cases, 10 to 20 per cent. of the volume of absolute alcohol are added. On cooling, the urethanes are separated off; for recrystallisation, Weehuizen uses the same petroleum fraction. With eugenol, it is advisable to carry out the reaction in solution with benzine of the b. p. 70 to 80° in the cold and to let the mixture stand for a couple of days in a closed vessel; the crystals of eugenol phenylurethane then are separated off.

By means of phenyl*iso*cyanate, borneol and camphor may be separated, both bodies being soluble in the petroleum fraction; on boiling, bornylphenylurethane is formed which crystallises out in the cold, whereas camphor does not react, and remains dissolved if sufficient of the solvent is present. With linalool and geraniol, no good results were obtained; especially in the case of linalool, much diphenylurea was formed.

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[1]) Comp. F. W. Semmler, *Berl. Berichte* **27** (1894), 2521; **34** (1901), 3128; *Report* April **1902**, 88. — [2]) *Rec. trav. chim. Pays-Bas* **37** (1918), 266. — Klages (*Berl. Berichte* **35** [1902], 2263) obtained the phenylurethanes of 1-propylol-4-methoxy- and -ethoxybenzene in ligroin solution, as Weehuizen remarks. Comp. also p. 20 of this *Report.*

The phenylurethanes obtained by Weehuizen showed the following melting points:— *o*-cresol, 141°; *m*-cresol, 121 to 122°, *p*-cresol, 121 to 123°; thymol, 106 to 107°, menthol, 111 to 112°; borneol, 137 to 138°; eugenol, 95°.

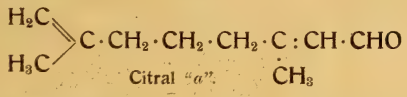
We beg to add that linalool phenylurethane may be obtained in the usual way without any difficulties.

The same object, *i.e.*. the identification of some terpene alcohols, is arrived at by means of the p-*nitro- and* p-*aminobenzoates*, the preparation and properties of which are given by S. V. Hintikka and L. Melander[1]). We take notice of their wook, because it seems not improbable that these compounds may be used for identifying these alcohols. The borneol ester of *p*-nitrobenzoic acid is obtained on heating 3 parts of borneol with 4 parts of *p*-nitrobenzoyl chloride; m. p. 134°[2]). In the same way, the *p*-nitrobenzoate of camphenilol is formed; the camphenilol used had m. p. 68 to 69°; $[\alpha]_D + 19.12°$. The fenchyl ester of the same acid was obtained on heating 4 parts of fenchyl alcohol and 5 parts of the acid chloride; m. p. 108 to 109°; the alcohol (prepared from fenchone) showed $[\alpha]_D - 8.43°$. On reducing bornyl *p*-nitrobenzoate with stannous chloride, tin and concentrated hydrochloric acid, bornyl *p*-aminobenzoate resulted; m. p. 144°; acetyl derivative, m. p. 158°. Camphenilyl *p*-aminobenzoate melts at 165°.

Attempts to prepare fenchyl *p*-aminobenzoate proved unsuccessful, since the fenchyl ester of *p*-nitrobenzoic acid resinified on reduction.

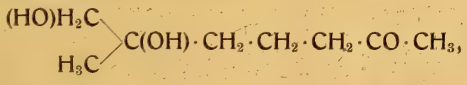
A. Verley[3]) has published a paper on the *constitution of geraniol, linalool, and nerol*, with which we wish to make our readers acquainted. We are, however, obliged to premise that Verley brings but few experimental details, so that it is difficult to form an opinion on the value of this work without after-examination.

The auther started from citral *"a"*, purified twice by means of the bisulphite compound, and boiled it with a 1 per cent. caustic soda solution,

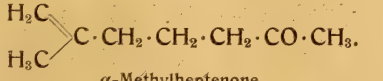


Citral *"a"*.

when he obtained a methylheptenone, b. p. 168°, which was different from Wallach's methylheptenone from cineolic acid anhydride of the b. p. 173 to 174°. The methylheptenone obtained by Tiemann from geraniol derivatives boiled from 171 to 172°. Verley's methylheptenone from citral *"a"*, on oxidation with potassium permanganate according to Tiemann and Semmler, yielded a glycol which, by further oxidation with



chromic acid gave merely traces of acetone, whereas synthetic methylheptenone gave about the theoretical quantity. Hence, Verley ascribes to his methylheptenone from citral *"a"*, which he terms α-methylheptenone, the following formula which is readily derivable from that of citral *"a"*:—



α-Methylheptenone.

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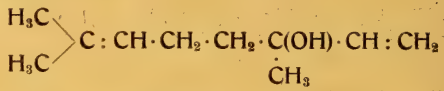
[1]) *Ann. Acad. Scient. Fenn., Ser.* A **10** (1919), No. 13; *Chem. Zentralbl.* **1919**, I. 836. — [2]) Comp. Henderson and Heilbron, *Proceed. chem. Soc.* **29** (1913), 81. — [3]) *Revue des produits chimiques* **21** (1918), 352.

Wallach's methylheptenone prepared "synthetically" from cineolic acid anhydride, b. p. 173°, was termed β-methylheptenone. The reason why Tiemann obtained β-methylheptenone from geraniol must be attributed, in Verley's opinion, to the use of sulphuric-chromic-acid mixture for oxidation, the sulphuric acid transforming the α-methylheptenone primarily formed into its β-isomeride, as may be proved by way of experiment. The latter differs from the former in the position of the double linking:—

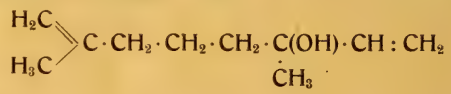
β-Methylheptenone.

From the reaction-product resulting from the action of hydrogen bromide, in glacial acetic acid solution, on geraniol, Verley abstracted HBr and obtained a new alcohol "*iso*linalool" which on oxidation yielded neral, and by boiling with acetic anhydride, neryl acetate. Purification of the *iso*linalool was effected by treatment of its iodine derivative with phthalic anhydride in presence of ether. The new alcohol boils at 200 to 210°; it smells sweeter than linalool and more rose-like; it is said to be contained in Mexican and in Cayenne linaloe oil. (From the inconstant boiling point it may be concluded that Verley dealt with an impure body.)

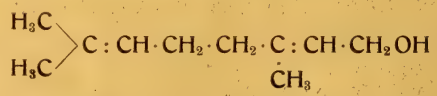


*Iso*linalool acc. to Verley.

By this it appears that this formula is one of the well-known formulæ for linalool. Ordinary linalool, according to Verley, would then be constituted as follows:—



When iodine is allowed to act on geraniol in a neutral solvent, only one molecule of hydrogen iodide is added; from the resulting product $C_{10}H_{19}OI$, on abstraction of HI, pure nerol is obtained. On theoretical grounds, Verley arrives at the following formula for nerol:—



The quite pure alcohol is stated to boil at 231 to 232° (ord. pressure), 124° (18 mm.).

Oxidation of nerol effected by shaking, in the cold, with very diluted chromic acid mixture leads to neral which was purified by means of its bisulphite compound; b. p. 120° (20 mm.); $d_{15°}$ 0.890. Its smell resembles that of citral, but is less lemon-like, and sweeter. Heating with 1 p. c. soda solution splits it up into acetaldehyde and β-methylheptenone.

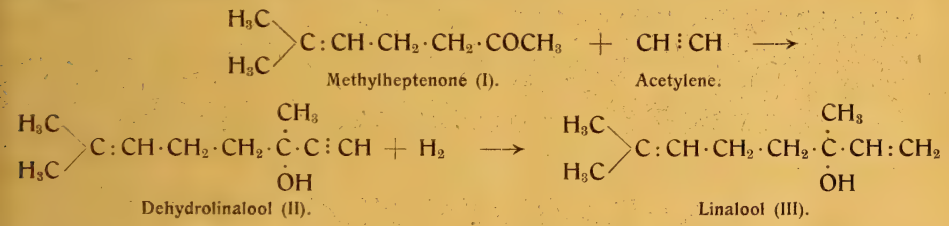
On shaking with a solution of cyanoacetic acid, neral dissolves after some time; after addition of sulphuric acid a brown oil is precipitated from the solution which solidifies soon and which consists of nerylidene cyanoacetic acid; m. p. 95°. Tiemann's compound prepared from citral "*b*" and cyanoacetic acid shows the same melting point.

Neral combines with acetone much slower than citral, with formation of the corresponding pseudoionone. Hence citral which in the manufacture of pseudoionone did not react with acetone gave, on reduction, a geraniol which was particularly rich

in nerol. Verley concludes, therefore, that lemongrass oil contains, in addition to citral *"a"*, about 6 to 7 per cent. of neral.

Citral *"b"* would then be the aldehyde neral corresponding to nerol.

A total synthesis of linalool. — The methods for preparing artificial linalool are all based on rearrangement reactions, no direct synthesis hitherto being known. Hence, inactive linalool was arrived at by starting from its isomeride geraniol, or from myrcene. A total synthesis has now been effected by L. Ruzicka and V. Fornasir[1]) who made use of Nef's[2]) reaction passing off between sodioacetylene compounds and ketones. They started from methylheptenone (I) obtained by Verley's method by boiling citral with soda solution (*vide* the preceding abstract), which they dissolved in absolute ether; then a suspension of sodium amide was added and a slow current of acetylene introduced into the well-chilled mixture. There resulted in a yield of 80 p.c., *dehydrolinalool* (II), a colourless limpid oil, reminding of the smell of methylheptenone and citral; b.p. 91 to 93° (12 mm.). The acetylene linking is evidently the reason why the pleasant smell of linalool does not manifest itself. In alcoholic solution the body gives a yellowish resinous precipitate on addition of ammoniacal silver nitrate. Its phenyl urethane melts at 88°. Reduction of dehydrolinalool to linalool (III) is effected by adding sodium to the ethereal solution of dehydrolinalool; when the evolution of hydrogen has ceased, water is added until the sodium is dissolved. The linalool resulting boiled at 86 to 88° (13 mm.); $d_{15°}$ 0.8649 and 0.8654; phenyl urethane, m.p. 63 to 65°.



Citronellol. — H. J. Prins[3]) undertook to separate citronellol into its isomerides by fractional distillation, but without success. He used in his experiments a citronellol obtained by reduction of citronellal which had been purified carefully by means of its bisulphite compound, as well as a citronellol resulting from its hydrate by steam-distillation in presence of sulphuric acid.

Prins ascribes the following constants for purest citronellol, *i.e.*, the mixture of the isomerides freed from geraniol, &c.: — $d_{\text{about } 100}$ 0.867 to 0.869, $n_{D20°}$ 1.4586 to 1.4589.

On p. 91 of our *Report* April **1915** we dealt with a paper by H. Meerwein[4]) on the reaction passing off in the transformation of borneol into camphene. This paper is now supplemented by a communication of the same author[5]), *on cyclic rearrangements occurring on splitting off water from alicyclic alcohols.*

In the first paper, Meerwein was able to prove that the atomic transposition occurring on transformation of borneol into camphene (Wagner's rearrangement)[6]) is not limited to the bicyclic borneol and related compounds, but likewise passes off in the same manner on abstracting water from monocyclic alcohols of similar structure.

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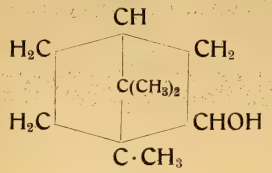
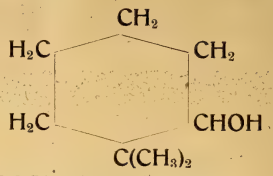
[1]) *Helvet. chim. acta* **2** (1919), 182. — [2]) *Liebig's Annalen* **308** (1899), 264. Compare also K. Hess and H. Munderloh, *Berl. Berichte* **51** (1918), 377. — [3]) *Chem. Weekblad* **15** (1918), 1378. — [4]) *Liebig's Annalen* **405** (1914), 129. — [5]) *Ibidem* **417** (1918), 255. — [6]) Compare p. 115 of this *Report*.

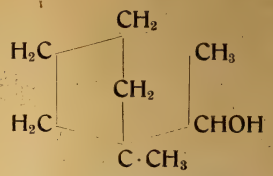
The simplest monocyclic alcohols resembling borneol in their structure (into which the bicyclic borneol may be so-to-say resolved) are 2.2-dimethyl*cyclo*hexanol-1 and 1.1-methyl-α-hydroxyethyl*cyclo*pentane:—



Borneol.

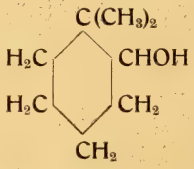


2.2-Dimethyl*cyclo*hexanol-1.

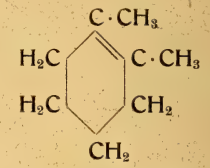


1.1-Methyl-α-hydroxyethyl*cyclo*pentane.

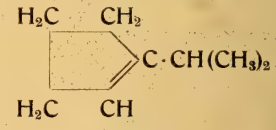
Formerly, Meerwein succeeded in obtaining the first-named alcohol only, and the results observed on splitting off water therefrom were insofar in accord with his expectations, that likewise with borneol, not the normal product of dehydration, 1.1-dimethyl-Δ^2-*cyclo*hexene, was obtained, but partly, with migration of a methyl group, 1.2-dimethyl-Δ^1-*cyclo*hexene, partly, with transformation of the hexacyclic into the pentacyclic nucleus, Δ^1-*iso*propyl*cyclo*pentene:—



2.2-Dimethyl*cyclo*hexanol-1.



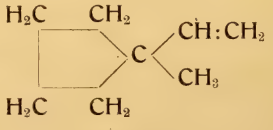
1.2-Dimethyl-Δ^1-*cyclo*hexene.



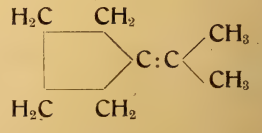
Δ^1-*Iso*propyl*cyclo*pentene.

Later on, Meerwein, in collaboration with C. Fleischhauer[1]), succeeded in synthesising 1.1-methyl-α-hydroxyethyl*cyclo*pentane. He started from *cyclo*pentanone, as is described below. On abstracting water from the alcohol, a reaction passing off particularly smoothly on heating with zinc chloride, a hydrocarbon results for which three formulæ come into consideration, according as the splitting off of water passes off without rearrangement (I), with migration of a methyl group (II), or with transformation of the pentacyclic system to a hexacyclic one (III):—

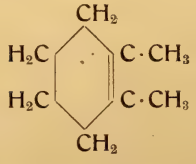
(I)



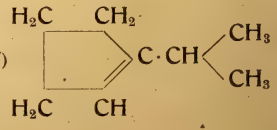
(II)



(III)



(IV)

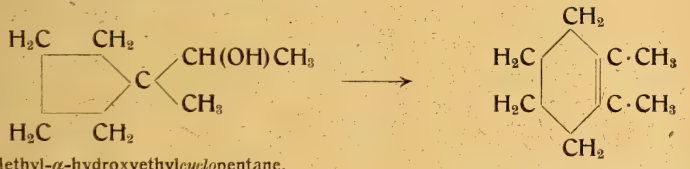


[1]) *Inaug.-Dissert.*, Bonn 1915.

In addition, there was to be expected that owing to the well-known great sensitiveness of hydrocarbons with semicyclic double bonds a transposition of the *iso*propylidene-*cyclo*pentane (II) into its isomeride, Δ^1-*iso*propyl*cyclo*pentene (IV), would take place under the influence of zinc chloride. Both the hydrocarbons (III) and (IV) are known, and it could be demonstrated without difficulty that the hydrocarbon from 1.1-methyl-α-hydroxyethyl*cyclo*pentane was nearly pure 1.2-dimethyl-Δ^1-*cyclo*hexene (III). It boils at 135 to 137° and smells feebly of terpenes. The nitrosochloride congeals only with difficulty and yields the nitrolpiperidide likewise difficultly; m.p. 120 to 121°. The hydrocarbon was identified by its dibromide (m.p. 140°) and by its physical properties. Δ^1-*Iso*propyl-*cyclo*pentene was not present in the *cyclo*hexene, in which case its presence would easily have been established by means of its difficultly soluble, stable nitrosochloride. Neither were any products obtained on ozonisation of the hydrocarbon, which would have pointed to the presence of *iso*propyl*cyclo*pentene. The neutral ozonisation product was pure 2.7-diketooctane: —

1.2-Dimethyl-Δ^1-*cyclo*hexene. 2.7-Diketooctane.

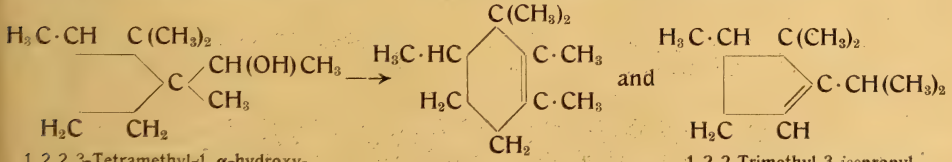
This dehydration from 1.1-methyl-α-hydroxyethyl*cyclo*pentane, with formation of 1.2-dimethyl-Δ^1-*cyclo*hexene, is perhaps one of the smoothest reactions leading from the *cyclo*pentane to the *cyclo*hexane series: —



1.1-Methyl-α-hydroxyethyl*cyclo*pentane. 1.2-Dimethyl-Δ^1-*cyclo*hexene.

In Meerwein's opinion, this easy transformation of a five-ring into a six-ring, also taking into consideration the ready passages of hexacyclic to pentacyclic systems, is a proof for the fact that in both systems there is no marked difference in the ring-tension.

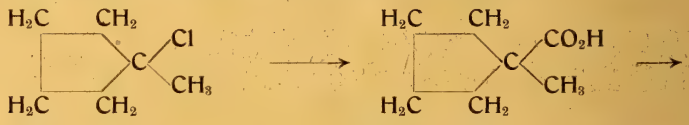
Strange to say, the abstraction of water from the homologues of 1.1-methyl-α-hydroxyethyl*cyclo*pentane does not pass off in one single direction. With 3-*iso*propyl-1.1-methyl-α-hydroxyethyl*cyclo*pentane, this phenomenon had been observed by Meerwein some time ago; in addition to 1.2-dimethyl-4-*iso*propyl-Δ^1-*cyclo*hexene, small quantities of 1.3-di-*iso*propyl*cyclo*pentene were formed. He now succeeded in proving that from 1.2.2.3-tetramethyl-1.α-hydroxyethyl*cyclo*pentane there were formed simultaneously, partly by extension of the ring system, partly with migration of a methyl group, 1.2.3.3.4-pentamethyl-Δ^1-*cyclo*hexene as well as 1.2.2-trimethyl-3-*iso*propyl-Δ^3-*cyclo*pentene: —



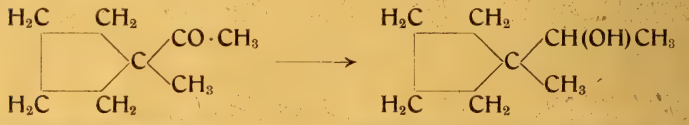
1.2.2.3-Tetramethyl-1.α-hydroxyethyl*cyclo*pentane. 1.2.3.3.4-Pentamethyl-Δ^1-*cyclo*hexene. 1.2.2-Trimethyl-3-*iso*propyl-Δ^3-*cyclo*pentene.

This different behaviour of the homologues may, in Meerwein's opinion, be ascribed to the fact (frequently observed) that the stability of the ring system, *i. e.*, its resistance towards cleavage, is increased by substitution.

Finally, we wish to give a short description of the method how 1.2.2.3-tetramethyl-1.α-hydroxyethyl*cyclo*pentane and 1.1-methyl-α-hydroxy*cyclo*pentane were prepared. Meerwein starts from 1.1-methylchloro*cyclo*pentane, the preparation of which he had published some time ago[1]), and brings it, in ethereal solution, into reaction with magnesium. The reaction having passed off, carbon dioxide is introduced into the mixture. The 1.1-methyl*cyclo*pentane carboxylic acid thus formed is converted into its chloride which by interaction with the stœchiometrical quantity of CH_3MgI, at low temperature[2]), yields a fair amount of 1.1-methylacetyl*cyclo*pentane; b. p. 48.4° (10 mm.); semicarbazone, m. p. 143 to 144°. It shows an intense smell recalling camphor and peppermint. The ethereal solution of the ketone is treated with sodium and then reduced by adding water drop by drop. The 1.1-methyl-α-hydroxyethyl*cyclo*pentane boils at 67.6° (10.5 mm.) and shows a characteristic peppermint-like and musty smell.



1.1-Methylchloro*cyclo*pentane. 1.1-Methyl*cyclo*pentane carboxylic acid.



1.1-Methylacetyl*cyclo*pentane. 1.1-Methyl-α-hydroxyethyl*cyclo*pentane.

For the preparation of 1.2.2.3-tetramethyl-1.α-hydroxyethyl*cyclo*pentane, Meerwein started from campholic acid (1.2.2.3-tetramethyl*cyclo*pentane carboxylic acid) resulting from heating camphor with caustic potash up to 250 to 270°. On interaction of the chloride of this acid with zinc methide or favourably with CH_3MgI, 1.2.2.3-tetramethyl-1-acetyl*cyclo*pentane is formed, a colourless oil with a pleasant smell reminding of pine needle oil; b. p. 101 to 102° (18 mm.); semicarbazone, m. p. 232°. On reduction with sodium and moist ether it yields 1.2.2.3-tetramethyl-1.α-hydroxyethyl*cyclo*pentane, a pleasantly smelling oil of the b. p. 108 to 109° (15 mm.). On cooling, this alcohol congeals partly and seems to consist of a mixture of two stereoisomeric modifications, a liquid and a solid one, the latter melting at 70 to 71°. The abstraction of water from this alcohol was effected by heating with zinc chloride. As is mentioned above, there are formed in this reaction 1.2.3.3.4-pentamethyl-Δ^1-*cyclo*hexene and 1.2.2-trimethyl-3-*iso*propyl-Δ^3-*cyclo*pentane. It was impossible to isolate any crystalline product from this mixture of hydrocarbons; the structure of the components was ascertained by ozonisation. The neutral products of this oxidation were two isomeric ketones $C_{11}H_{18}O$, in all probability 1.2.2.3-tetramethyl-4-acetyl-Δ^3-*cyclo*pentene and 1.2.3.3-tetramethyl-4-acetyl-Δ^1-*cyclo*pentene, both resulting from hydroxyketones formed intermediately. The acid product was a ketonic acid $C_{11}H_{18}O_3$ originating from 1.2.2-trimethyl-3-*iso*propyl-Δ^3-*cyclo*pentene.

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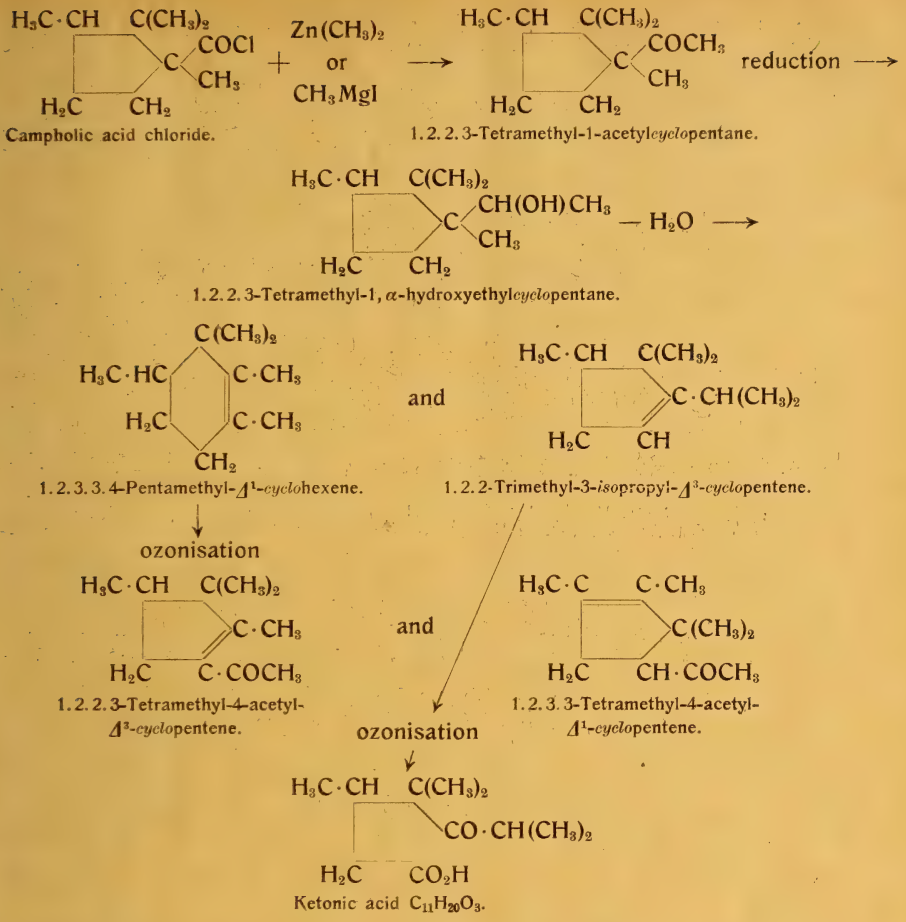
[1]) *Liebig's Annalen* **405** (1914), 170. — [2]) Following a method of Grignard and Rost, *Compt. rend.* **153** (1911), 772.



Camphyl carbinol and other reduction products of hydroxymethylene camphor. — By means of a process patented some years ago[1]) it is possible to reduce hydroxymethylene camphor, with sodium and alcohol, to camphyl glycol. Later on, Kötz and Schaeffer[2]) hydrogenated hydroxymethylene compounds by means of colloid palladium or platinum according to Paal's and Skita's directions and observed a very interesting formation of methyl ketones. As a by-product, there could be isolated, on reduction of hydroxymethylene dihydrocarvone, a poor yield of the ketonic alcohol which was obtained as benzoyl compound. With hydroxymethylene camphor, no reduction could be effected with hydrogen in presence of palladium or platinum.

Basing on these experiments, H. Rupe, A. Akermann and H. Takagi[3]) succeeded in reducing hydroxymethylene camphor, by means of hydrogen and nickel at room temperature and under ordinary pressure, to the ketonic alcohol *camphyl carbinol* (II). However, the reaction proceeded very slowly and the reduction was incomplete when finely-divided nickel powder was employed. The reduction passes off far better if a mixture of clay-and-nickel powder is used. For this purpose, pieces of porous clay plates are ground

[1]) Germ. Pat. 123909. — [2]) *Berl. Berichte* **45** (1912), 1952. — [3]) *Helv. chim. acta* **1** (1918), 452.

to a most fine powder which is mixid with aqueous nickel sulphate solution so as to form a thin paste, then treated with the calculated amount of caustic soda solution, boiled up after addition of water, and poured in cold water. The liquid was decanted from the precipitate and the latter washed out in a centrifugal until the washing water showed no more alkaline reaction. Finally, the precipitate was dried at 140° and ground to an exceedingly fine powder. For reduction, the authors used a simple electric furnace built of a copper tube surrounded by a resistance coil and further by a wider black-iron pipe, the space between both being filled with kieselgur (diatomite). A glass tube was inserted in the copper tube and filled to about one-half with 100 to 120 g. of the clay-nickel-powder. For heating, monophasic alternating current of 110 volts was used, the most favourable temperature for the reduction being about 370 to 380°. The glass tube was closed at both ends with india-rubber stoppers permitting of conducting the hydrogen current in either direction alternately. A skilful contrivance enabled continual shaking the powder in the tube to and fro. Complete reduction of 120 g. of the clay-nickel-powder took 46 to 60 hours. The cooling is carried out in the beginning in a current of hydrogen, later on in carbon dioxide. The powder thus obtained catches fire on exposure to the air and burns down gradually. In sealed glass tubes filled with carbon dioxide, the powder may be kept a fairly long time, apparently without losing much of its activity.

For reduction, the hydroxymethylene camphor is dissolved in 10 to 50 times its weight of 50 p.c. alcohol, or its neutral sodium salt is dissolved in water. For one part of the preparation, two parts of the nickel powder are used. Hydrogen is then introduced under an excess pressure of about 1.30 m. water column. The freshly-prepared pyrophoric nickel powder reduces water rather violently. The hydrogenation carried out, the alcohol is driven over by steam and the residual aqueous solution, together with the nickel-and-clay powder is carefully extracted with ether. The yield amounts to 80 to 95 p.c. of the theory. Camphyl carbinol boils at 139 to 140° (9 mm.); $d_{4^\circ}^{20^\circ}$ 1.0502. It is a colourless and odourless liquid, the vapours of which smell faintly camphoraceous. The taste is bitter and burning. Purification of the camphyl carbinol is effected best by means of its calcium chloride compound. On treatment with PBr_3 it yields the hydrobromide, camphyl bromomethane (III), a pleasantly-smelling body melting at 65.5 to 66° and crystallising in long, white, flat needles. The hydrochloride, camphyl chloromethane (from camphyl carbinol and $SOCl_2$) melts at 53 to 54°.

On oxidising camphyl carbinol with chromic acid in glacial acetic acid solution, camphor quinone (m.p. 197°) resulted. Oxidation with sulphuric acid and manganese dioxide led to a minute amount of a body melting at 201°.

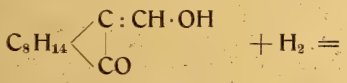
The benzoyl compound of camphyl carbinol is prepared best by shaking the carbinol with benzoyl chloride in pyridine solution; m.p. 95 to 97°. Attemps to saponify the ester had not the effect desired, since the carbinol splitted off water and formed methylene camphor (V). Comparatively the best way for saponification was the treatment with acids. Camphyl carbinol obtained in this manner showed $[\alpha]_{D20^\circ} + 65.73^\circ$, the same purified by distillation $[\alpha]_D + 62.11^\circ$ and from the calcium chloride compound $[\alpha]_D + 62.22^\circ$. In the authors' opinion, the camphyl carbinol obtained by saponifying the benzoate may, for the present, be considered to be optically pure.

By treatment with formic acid, camphyl carbinol is converted into a formyl derivative (IV), m.p. 74 to 75°, b.p. 142 to 143° (11 mm.). It is noteworthy that camphyl carbinol, otherwise so sensitive, is in this case readily esterified and loses no water. With acetic anhydride, the acetate is formed, a pleasantly smelling oil, b.p. 148.5 to 149° (10 mm.).

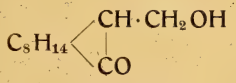
When hydroxymethylene camphor is hydrogenated, several by-products are formed, *inter alia*. *methylene camphor* (V), a very volatile substance with a strong, camphoraceous smell. On treatment with hydrobromic acid in glacial acetic acid solution, camphyl bromomethane (III) results. With bromine in chloroform solution, methylene camphor yields the dibromide, m.p. 108 to 109°.

On abstracting hydrogen bromine from camphyl bromomethane by means of methyl-alcoholic potash, or better on heating camphyl carbinol with alcoholic potash, chemically pure methylene camphor is obtained; m.p. 43.5 to 44°; b.p. 85 to 85.5° (9 mm.). The preparation obtained by Minguin[1]) on boiling bromomethyl camphor with alcoholic potash (m.p. 30 to 35°) was but impure.

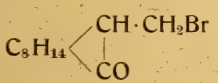
From methylene camphor, there resulted, on hydrogenation, as by-product *methyl camphor* (VI) which may be separated from methylene camphor by converting the latter into its hydrobromide and extracting the methyl camphor from the filtrate of the hydrobromide with ether. It is obtained in the purest state by reducing methylene camphor; m.p. 37.5 to 38.5°; b.p. 88 to 89° (8.5 mm.).



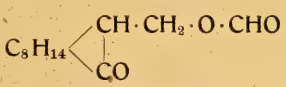
(I) Hydroxymethylene camphor.



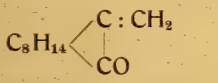
(II) Camphyl carbinol.



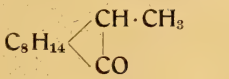
(III) Camphyl bromomethane.



(IV) Formyl derivative of camphyl carbinol.



(V) Methylene camphor.



(VI) Methyl camphor.

The authors explain the formation of methylene camphor as a by-product by means of the dehydrating action of the nickel powder on a small part of the camphyl carbinol formed.

A by-product fraction, b.p. 88 to 110° (10.5 mm.) yielded, on treatment with methyl alcoholic potash, methylene camphor and methyl camphor. The authors are of opinion that in this case methylene camphor is formed by splitting up of the ethyl ether of camphyl carbinol which in turn resulted from the addition of ethyl alcohol to methylene camphor.

Another by-product fraction, b.p. 110 to 138° (10.5 mm.), yielded on boiling with alcoholic potash methylene camphor and hydroxymethylene camphor, and the authors suspect, therefore, amongst the by-products also the ethyl ether of hydroxymethylene camphor, whose formation is due to a condensation, under the influence of nickel, of hydroxymethylene camphor and ethyl alcohol.

A. Tschirch[2]) gives a retrospective review on the present knowledge concerning *resinols* and *resinotannols*. Towards the end of his noteworthy publication the author advances the opinion that the resinotannols are not protoretines, but teleutoretines and correspond to the final bases, saponines, and other products resulting from primarily-formed bodies. From the view of the evolution doctrine, the resinotannols follow the

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[1]) *Compt. rend.* **136** (1903), 752. — [2]) *Schweiz. Apoth. Ztg.* **57** (1919), N^os^ 5 and 6.

resinols, a fact correctly recognized already by Reinitzer. The quality of tanning is very different with the various resinotannols; with some of them, the reactions for tanning matter are but very indistinct. In any case, they do not range with the tans proper.

We beg to add that Tschirch had, at a time, found the resinotannols in tannol resins and characterised them as resin alcohols. The coloured ground-mass of *e. g. Benzoe amygdaloides* contains tannol esters, the colourless substance of the "tears", however, is for the first free from these esters, but not the surrounding outer coating.

Aldehydes.

Reduction of aldehydes and ketones by biological means. — We have repeatedly, in our *Reports*[1]), referred to the interesting phytochemical reduction of aldehydes and ketones effected by Neuberg and his collaborators by action of yeast. Recently, Neuberg and M. Ringer[2]) succeeded in hydrogenating, by phytochemical means, and in asymmetrical way, racemic valeric aldehyde (*d,l*-methylethylacetaldehyde) to *l*-amylalcohol. The aldehyde was prepared according to Claisen's method[3]) and the directions given by V. Neustädter[4]) by condensing methyl ethyl ketone (I) with ethyl chloroacetate (II) in presence of sodium amide. From the resulting methyl ethyl glycidic ester (III) the free acid (IV) was obtained *via* the sodium salt, the acid, as well as the corresponding dihydroxy acid (V), yielding on distillation or on boiling the aldehyde (VI) with evolution of carbon monoxide.

In the first experiment, the aldehyde was brought together with a solution of cane sugar and fresh yeast, brand "OM". After five days, the fermentation was finished. The amylalcohol thus obtained boiled at 129°; the rotation (α_D — 0.45°) corresponded to a content of about 10 p. c. lævorotatory amyl alcohol. The yield was 7.5 g. from 14 g. methyl ethyl acetaldehyde. Since the phytochemical reductions pass off particularly well with the aldehydo-ammonia compounds, a second experiment was carried out with *d,l*-valeric aldehyde in presence of ammonia, when a better yield was obtained, *i.e.*, 12.4 g. amyl alcohol from 17.2 g. valeric aldehyde = about 70 p. c. of the theoretical amount. The rotation was — 0.941°, answering to about 16 p. c. of the lævorotatory alcohol. A trial test showed that on fermenting cane sugar alone with fresh top yeast "M" but such a minute quantity of amyl alcohol results that it may be negleacted entirely.

In a like manner Neuberg in community with A. Lewite[5]), effected the reduction of methyl heptenone (VII) to methylheptenol (VIII), although as a rule the ketones cannot be reduced phytochemically. The reduction-product, differing from the ketone by its asymmetric carbon atom, was optically active. It was remarkable that in a course of fermentations the methylheptenol showed a changing rotation, a phenomenen which hitherto could not be explained, although an analogous reaction is known, where a ketone, under biochemical influence, yields at one time a certain reaction-product, at another time a different one, *i.e.*, the conversion by animal organs of methylglyoxal into *d*- or *l*-lactic acid. In no case did the yield of methylheptenol exceed 10 p. c.

The fermentation liquid contained acetaldehyde, the formation of which was doubtless connected with the fermentation process, as its quantity was in proportion to the methylheptenol formed. Evidently, the hydrogenation of methylheptenone is allied to the formation of acetaldehyde. The authors are of opinion that a sort of competition

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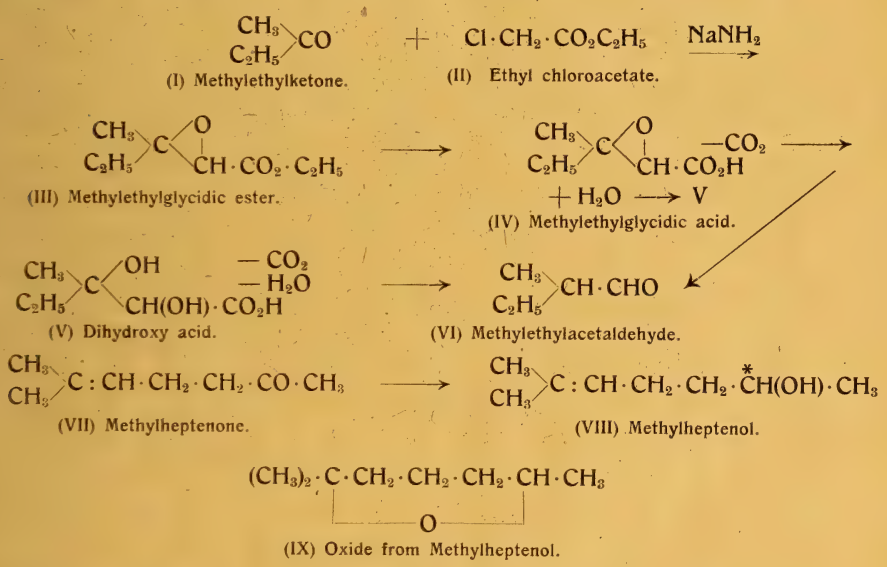
[1]) Comp. *inter alia, Report* April **1915**, 91; October **1916**, 120. — [2]) *Biochem. Zeitschr.* **90** (1918), 388. — [3]) *Berl. Berichte* **38** (1905), 707. — [4]) *Monatsh. f. Chem.* **27** (1906), 888. — [5]) *Biochem. Zeitschr.* **91** (1918), 257.

takes place, between the acetaldehyde formed as intermediate and the ketone added, for the hydrogen which in the last stage of the fermentation-process effects the regular hydrogenation down to ethyl alcohol. Hence, just so much of the acetaldehyde escapes reduction as corresponds to the ketone reduced. Naturally, it is here the question of an equilibrium, limited by the tendency to pass off within the normal course of alcoholic formentation.

Methylheptenone has a decidedly unfavourable action upon the fermentation-process, more especially the fermentation velocity is retarded considerably. This results in the fact that an excess of the ketone is able to lock out, up to a certain degree, the intermediate acetaldehyde from normal hydrogenation. Hence, with methylheptenone, the hydrogenation passes off at the expense of the fermented sugar.

In order to identify the methylheptenol, the authors converted it into the isomeric oxide (IX) described by Wallach[1]) and by Rupe and Schlochoff[2]) and giving a well-defined addition product with hydrogen ferricyanide.

For identification of methylheptenone, Neuberg and Lewite recommend to prepare the *p*-nitrophenylhydrazone forming light-yellow needles, m. p. 103.5 to 104°.



Neuberg and Kerb[3]), when reporting on the reduction of citral to geraniol by means of yeast, deal also with the preparation of *cyclo*citral and some crystallised derivatives thereof.

On biochemical reduction, citral is reduced in the main to geraniol, a small proportion is converted into an optically active alcohol, concerning the nature of which nothing positive could yet be stated. In any case, it is not the question of linalool.

For carrying out the reaction, a regular fermentation process is not necessary, the reduction passing off equally well on digesting citral with yeast alone.

The geraniol was identified by its calcium chloride compound and its acid phthalate, the silver salt of which was analysed; m.p. 131 to 132°.

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[1]) *Liebig's Annalen* **275** (1893), 171. — [2]) *Berl. Berichte* **38** (1905), 1498. — [3]) *Biochem. Zeitschr.* **92** (1918), 111.

On treatment of commercial geraniol with yeast, small quantities of optically active bodies are formed, and simultaneously the capacity of adding bromine is diminished, possibly indicating either formation of *cyclo*geraniol or reduction to citronellol.

An experiment started in the usual way with *cyclo*citral and fermenting yeast gave rise to a mixture of substances in which unchanged *cyclo*citral predominated by far. In addition, a small amount of an alcoholic product resulted, the nature of which could not be explained.

Finally, Neuberg and Kerb report on some new crystalline derivatives of *cyclo*citral: thiosemicarbazone, m.p. 200 to 201°; *p*-nitrophenylhydrazone, m.p. 125°.

Furthermore, we beg to report on a paper by Neuberg[1]) entitled, "*A general relation of the aldehydes to alcoholic fermentation.* with remarks on the co-ferment of yeast".

The auther points out that the enzyme "carboxylase" contained in the grouping of ferments comprised in the collective name of zymase, exerts a very high activity, since it produces not alone the fermentative carbonic acid, but also aldehydes. The material yielding the aldehydes are α-ketonic acids which, in the present view, are the primary reaction-products in the animal and vegetable organism of the α-amino acids. Hence, the carboxylase is one of the ferments serving to bring the degradation products of albumen into reaction. The aldehydes which are so widely distributed, although in minute quantities, may be considered as resulting from the action of the carboxylase. Quite recently, other relations of the system: carboxylase — α-ketonic acid to the important process of intramolecular respiration have been discovered, of which the example best known is the alcoholic fermentation. Neuberg and his collaborators have found that traces of α-ketonic acids of physiological importance activate the process of sugar-fermentation in a marked degree.

Neuberg was now able to demonstrate that the aldehydes count amongst the most effective activators for alcoholic fermentation and in molecular respiration. With 38 aldehydes, aliphatic and aromatic, Neuberg proved the stimulating action beyond doubt.

The aliphatic aldehydes, from formaldehyde to decylic aldehyde, gave a positive reaction, equally so benzaldehyde and its homologues, the hydroxybenzaldehydes and their ethers of the anisic aldehyde and piperonal type, also phenylacetic aldehyde, citronellal, citral, *cyclo*citral, and cinnamic aldehyde. The only exception was vanillin (*m*-methoxy-*p*-hydroxy-benzaldehyde), where no activating effect could be traced; in this case, however, the concentration may not have been the correct one.

The activating power of the aldehydes manifests itself in the fermentation of *d*-glucose, *d*-fructose, and *d*-mannose, and their action comprises a very wide range of concentration, the same aldehyde showing the same effect in dilutions differing by 1 : 1000 (standard solution and $\frac{1}{1000}$ standard solution). The active quantities may differ even in the ratio of 5000 : 1, as is shown by the activating power of 1.17 p.c. citral in the sugar solution and of the exceedingly low content of 0.00023 p.c. of formaldehyde.

The strong stimulating influence of the aldehydes shows itself particularly when grape sugar (dextrose) is fermented. The action of the aldehydes presents itself best on fermenting the sugar with the maceration-juice from yeast in the ordinary way, *e.g.*, on treating a 5 p.c. sugar solution with the five-fold amount of fermentation-liquid. Tho this mixture, the aldehyde solutions are added in varying dilutions. The activating power is observed best when the fermentation tests are carried out in a eudiometer.

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[1]) *Biochem. Zeitschr.* 88 (1918), 145.

The beneficial influence of the aldehydes is strictly limited to this class of bodies and is entirely missing with the ketones. Hence, the addition of any bodies interfering with the aldehydic character destroy the stimulating action.

The effect of the activating action of the aldehydes is the same as results from raising the temperature, *i.e.*, the aldehydes accelerate fermentation in the same manner as does gentle heating. If one considers that, according to the rule of van't Hoff, a raise in the temperature by 10° usually doubles the reaction velocity, one may easily judge the effect of the stimulating action of the aldehydes which without alteration of the temperature are able to accelerate the reaction by the 100-fold amount.

Since this activation passes off at low temperatures as well as at room temperature, it may be regarded as a means of the plant for rendering the necessary intensity of the respiration and hence the increase in energy independent of the surrounding temperature. Other phytophysiological processes may likewise be explained by the action of the aldehydes; for instance, any rise in the formation of aldehydes is possibly followed by an increase, and any rise in the consumption of aldehydes by a decrease, of the respiration — in short, the aldehydic metabolism influences the speed of phytophysiological respiration.

The following aldehydes were investigated: —

Aliphatic aldehydes: — formaldehyde, propionic, *n*- and *iso*-valeric, *d*-valeric, *d,l*-methylethylacetic, *n*-capronic, œnanthic, octylic, nonylic, and decylic aldehydes;

Halogenated aldehydes: — chloral hydrate;

Hydroxy aldehydes: — aldol, acetopropionic aldol;

Unsaturated aldehydes: — citronellal, citral;

Aromatic aldehydes: — benzaldehyde, cuminic, phenylacetic aldehydes;

Aromatic hydroxyaldehydes and their ethers: — salicylic, *p*-hydroxybenzoic, anisic aldehydes, piperonal, vanillin;

Unsaturated aromatic aldehydes: — cinnamaldehyde;

Cyclic aldehydes: — furfural, *cyclo*citral;

Dialdehydes: — glyoxal, *iso*- and terephthalic aldehydes;

Ketonic aldehydes: — methyl and phenyl glyoxal;

Aldehydo acids: — aldehydosuccinic, *o*- and *iso*-phthalaldehydo acids, opianic acid.

Generally, the aldehydes were dissolved in absolute alcohol and then diluted with water. The solutions were either clear or faintly turbid; on mixing with the yeast extract and the sugar solution, always nearly quite clear mixtures resulted.

How the aldehydes acted under various conditions appears from the author's abstracts of the experimental details.

In experiments with fresh maceration juice from dry yeast of March 1915 and dextrose (t_{180}; 10 cc. juice; 2 cc. 5 p.c. dextrose solution), the following results were obtained: —

CO_2 development after	30 min.	60 min.	90 min.	120 min.	18 hrs.
with 1 cc. 12.5 p.c. alcohol	0	0.4	7.2	9.0	17.5
„ 1 „ m/100 propionic aldehyde . .	0.5	3.2	7.7	9.2	19.1
„ 1 „ „ *iso*butylic „ . .	2.0	7.5	9.5	10.5	19.0
„ 1 „ „ *iso*valeric „ . .	4.5	7.0	9.4	10.7	18.6
„ 1 „ „ *n*-capronic „ . .	3.2	4.7	7.4	9.2	17.8
„ 1 „ „ œnanthic „ . .	5.5	8.0	9.7	10.7	16.1

The marked action of the last-named aldehyde is of special interest.

In experiments with the same juice from dry yeast of March 1915 which was kept standing for 24 hours, and with dextrose, cinnamaldehyde proved to be exceptionally active, the action excelling by far that of the other aldehydes. A comparative test with methyl *n*-hexyl ketone showed that this body acted not only slower than the isomeric octylic aldehyde and, in general, all other aldehydes, but also slower than a blank test with water; hence, thn ketone rather seemed to retard the reaction.

In experiments with fresh juice from dry yeast of March 1916 and dextrose, furfural and anisic aldehyde proved to be particularly effective.

Likewise, with fresh juice from yeast of September 1916 and dextrose, piperonal, cuminic aldehyde, and the phthalic dialdehydes manifested themselves as powerful stimulants; of the phthalic aldehydoacids, the *ortho* compound was without action, possibly because the so-called *o*-phthalaldehydo acid contains no aldehydo group, but reacts as the tautomeric γ-hydroxylactone.

Experiments with juice, 24 hours old, from yeast of September 1916, dextrose, and ketones were negative, as was the test with methyl *n*-hexyl ketone.

From an experiment with fresh juice from dry yeast of September 1916 and dextrose, with addition of propionic aldehyde in various concentrations, and at low temperature (11 to 12°) it was found that with the simple aldehydes, the most favourable concentration for bringing about the activity is, in general, near the concentration $\frac{m}{100}$.

These experiments were followed by comparative tests with fresh juice from dry yeast of September 1915 and dextrose and with equimolecular quantities of such aldehydes as were considered to be typical representatives of each series; the rise in the fermentation-speed observed on addition of the aldehydic activators to the various mixtures was found to range between 800 and 1200 p.c.

On activating the dextrose fermentation-process by means of different typical aldehydes added in molecular concentration all the aldehydes investigated (with exception of formaldehyde, which in this concentration stops the fermentation) manifested their activating effect, *e. g.*, after 30 minutes or one hour. With benzaldehyde and *iso*valeric aldehyde, however, the activation was retarded at the beginning of the second hour, nevertheless, furfural and œnanthol showed their beneficial influence under these abnormal conditions. In a mixture of 13 g., a content of 0.1552 g. of the high-molecular citral is strongly active.

When activating the fermentation of dextrose with typical aldehydes in $\frac{m}{10}$ concentration, the strong action of formaldehyde was striking.

In the fermentation of mannose, the simple aldehydes and dialdehydes, in accord with the results observed on fermenting dextrose proved likewise to be fully effective. Mannose is particularly suited for studying the stimulating action, as under the conditions ruling its fermentation proceeds somewhat slower than with dextrose.

Comparative tests, at 18.5°, with juice from dry yeast and a 5 p.c. solution of levulose showed no noticeable effect on addition of aldehydes in $\frac{m}{10}$ concentration. In the mixtures with $\frac{m}{10}$ furfural, $\frac{m}{10}$ acetaldehyde, and $\frac{m}{10}$ œnanthol, fermentation began nearly instantaneously, but the differences disappeared soon; on the other hand, formaldehyde, in $\frac{m}{10}$ concentration, retarded the vivid fermentation of the pure levulose solution. The author therefore lowered the temperature as well as the strength of the activators and diluted at the same time the yeast juice with 100 p.c. water. The activation was not very marked, yet sufficient so as to remove any doubts on the possibility of activating the fermentation of levulose.

With cane sugar, the proof of the activating effect, in accord with its rapid initial fermentition, is brought about best at low temperature and by using a yeast juice diluted to half its strength.

Addition products of aromatic aldehydes. — We report below, without entering into experimental details or theoretical discussions, on a spacious paper by H. Meerwein[1]) in which some interesting reactions are dealt with of bodies being of special interest for us.

Addition of desoxybenzoin (benzylphenylketone) to *cinnamic aldehyde* takes place when the solution of these bodies in methyl alcohol is treated, at reduced temperature, with sodium methoxide. The aldehydes resulting, *β-phenyl β-desyl propionic aldehyde,*

$C_6H_5 \cdot CH \cdot CO \cdot C_6H_5$
$C_6H_5 \cdot CH \cdot CH_2 \cdot CHO$

melts at 176.5 to 177°. Its constitution was proved by its oxidation to the corresponding acid (dehydroamaric acid) which could be prepared by synthesising desoxybenzoin with benzalmalonic ester and subsequent saponification and splitting-off of CO_2. On adding a solution of sodium in methyl alcohol to a cold solution of *cinnamic* and *phenylacetic aldehydes,* the latter turns yellow.

When sodium methoxide is added again after the smell of phenylacetic aldehyde has disappeared, and the solution, after some standing, is heated gently under a reflux condenser, the primary addition-product, *α, β*-diphenylglutaric aldehyde, is transformed into *β, γ-diphenyl valerolactone;* m. p. 123 to 123.5°, which

$C_6H_5 \cdot CH \cdot CH_2 \cdot O$
$C_6H_5 \cdot CH \cdot CH_2 \cdot CO$

on treatment with $KMnO_4$ is oxidised to *α, β*-diphenylglutaric acid; methyl ester, m. p. 84 to 85°. This acid occurs also in a stereoisomeric modification of indistinct melting point.

On addition of phenylacetic aldehyde to benzylidene acetophenone, primarily *α, β, δ*-triphenyl-*δ*-keto-*n*-valeric aldehyde is formed which on heating is rearranged into *α, β, δ*-triphenyl valerolactone. The corresponding acid, *α, β, δ*-triphenyl-*δ*-hydroxy-*n*-valeric acid, m. p. 143 to 143.5°, is stable; on heating up to 150° *in vacuo* it is reconverted into the lactone, m. p. 138 to 139°.

$C_6H_5 \cdot CH \cdot CO$
$C_6H_5 \cdot CH \cdot CH_2 \cdot CH \cdot C_6H_5$ (O)

$C_6H_5 \cdot CH \cdot CO_2H$
$C_6H_5 \cdot CH \cdot CH_2 \cdot CH(OH)C_6H_5$

On adding phenylacetic aldehyde to ethyl benzylidene acetoacetate, in ethylalcoholic solution, by means of sodium ethoxide a mixture of a difficultly and a readily soluble product is formed. The former is *α, β*-diphenyl-*γ*-carbethoxy-*δ*-keto-*n*-capronic aldehyde; m. p. 149°.

$C_6H_5 \cdot CH \cdot CH \cdot C_6H_5$
$C_2H_5OCO \cdot CH \quad CHO$
$CO \cdot CH_3$

α, β-Diphenyl-*γ*-carbethoxy-*δ*-keto-*n*-capronic aldehyde.

The readily soluble body is a product of a rearrangement of the former one.

The addition-product of phenylacetic aldehyde and ethyl benzylidene acetoacetate is split up on distillation *in vacuo,* but, strange to say, not again into its original components, but to *α*-phenylcinnamic aldehyde and ethyl acetoacetate.

α-Phenylcinnamic aldehyde was prepared synthetically by Meerwein according to Claisen's direction's given for such condensations: — shaking of a mixture of phenylacetic aldehyde, benzaldehyde, water, and potash solution —; m. p. 94°; oxime, m. p. 165 to 166°; phenylhydrazone, m. p. 125 to 126°.

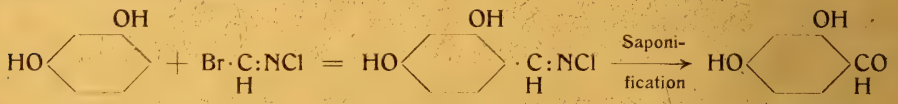
The addition-product from phenylacetic acid and ethyl benzylidene acetoacetate adds, on treatment with alcoholic hydrogen chloride, the elements of alcohol forming

[1]) *Journ. f. prakt. Chem.* II. **97** (1918), 225.

a readily soluble compound $C_{23}H_{28}O_5$, m. p. 79 to 81°. On distillation *in vacuo*, the body loses one molecule of water and yields a compound $C_{23}H_{26}O_4$, m. p. 129 to 130°.

A publication by S. Bodforss[1]) on *condensation-reactions of ketones* deals, *inter alia*, with the condensation of benzaldehyde with chloracetic anilide and of cuminic aldehyde with acetophenone by the action of aicoholates. Benzaldehyde yields phenylglycidic acid anilide, m. p. 142°. Cuminaldehyde, on condensation with acetophenone, gave rise to cuminalacetophenone which boiled at 225 to 227° (15 mm.) with slight decomposition and which, not being quite pure, even after some years standing showed no tendency to crystallise. The dibromide melted at 119 to 119.5°.

A *new synthesis of hydroxy aldehydes* is published by P. Karrer[2]). As the reaction may be of special interest for our branch of industry we wish to inform our readers about it. Karrer expected to arrive at carboxylic acids or at ketones when treating polyvalent phenols, in presence of hydrochloric acid, with cyanogen bromide. The result, however, was a very good yield of aldehydes. Resorcinol, for instance, in absolute ethereal solution, yielded with cyanogen bromide in presence of zinc chloride, on introducing hydrogen chloride, 2 : 4-dihydroxybenzaldehyde (resorcylic aldehyde), m. p. 135°, evidently according the equation: —



Resorcinol. Intermediate product. Resorcylic aldehyde.

In the same way, the author prepared, from phloroglucinol, phloroglucylic aldehyde, m. p. 105°.

We reported, on a previous occasion[3]), on the *occurrence of salicylic adehyde and vanillin in soils*. A paper by J. J. Skinner[4]) brings new details on the influence of these and some other aldehydes on the growth of plants. The author investigated 74 soils of which 14 were garden soils and 60 field soils; of these latter 30 were classed as productive and 30 as unproductive. Of the 14 garden soils, 5 contained aldehydes, and of the 60 field soils aldehydes were present in 12, these being divided amongst the productive and the unproductive soils in the proportion of 1 : 3. Besides the action of the the two aldehydes mentioned above, Skinner investigated the influence of benzaldehyde, piperonal, formaldehyde, and paraformaldehyde on the growth of plants in water and in nutrient-culture solutions, and of salicylaldehyde and vanillin in pot and field trials. Sixty-six culture solutions were used containing varying proportions of sodium nitrate, calcium superphosphate, and potassium sulphate. All of the aldehydes were found to be harmful in aqueous solutions in comparatively small amounts. Salicylaldehyde was less harmful when the solutions contained a high percentage of phosphate, and its effect was lessened somewhat by the presence of calcium carbonate. Vanillin was less harmful than salicylaldehyde. It affected the roots more severely than the tops of the plants. Its harmful effect was much lessened by the presence of sodium nitrate in considerable amount. Benzaldehyde when present to the extent of 25 parts per million was injurious to plant growth, and in this case there was no very marked beneficial influence exerted by any of the nutrient salts. Piperonal was much more

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[1]) *Berl. Berichte* **52** (1919), 142. — [2]) *Helvet. chim. acta* **2** (1919), 89. — [3]) Comp. *Report* April **1915**, 61. — [4]) *Journ. Franklin Inst.* **186** (1918), 165, 289, 449, 547, 723; *Journ. Soc. chem. Industry* **38** (1919), A. 83.

harmful than benzaldehyde and the plants were so severely injured that it was difficult to differentiate is effects in the different solutions.

From the pot and field trials it was found that salicylaldehyde and vanillin had no harmful action on well-drained, good productive soils in a high state of cultivation, which, when examined in the laboratory, were found to possess good oxidising power. Further in these soils, the aldehydes disappeared. The soils in which the aldehydes were found to have a harmful effect had a lower crop-producing power and their general management had not been so good. The aldehydes remained in these soils. In these latter soils lime and manganese salts greatly aided in lessening the effects of both aldehydes, phosphates ameliorated the harmfulness of salicylaldehyde and nitrate, of vanillin. Unfertile soils, poor owing to the presence of aldehydes, can be made productive by good drainage and by the use of lime and certain fertilisers.

The *piperylhydrazones of some aldehydes* of special interest for us have been described by A. Weinhagen[1]). The piperylhydrazine employed was prepared by reducing nitrosopiperidine[2]). The hydrazones were obtained by heating the aldehydes with the requisite amount of piperylhydrazine in alcoholic solution faintly acidified with acetic acid. The piperylhydrazone of piperonal melted at 65 to 67°, of salicylaldehyde at 71 to 72°, of benzaldehyde at 68 to 69° (Knorr giving 62 to 63°, and Forster[3]) 68°), and of anisic aldehyde at 54°. When preparing the last-named hydrazone, a reddish-violet impurity was formed which, however, was insoluble in light petroleum and could be easily removed from the reaction-mixture by extraction with that solvent, in which the hydrazone is readily soluble.

Citral. — Knoevenagel, in an extensive publication[4]), reports on the condensation of citral with ethyl acetoacetate. The condensation passes off with elimination of water, according to the experimental conditions by union of equal molecules of citral and ester, with formation of citrylidene acetoacetic ester, or of one molecule of citral with two molecules of ester, forming citrylidene *bis*-acetoacetic ester.

Isomerism as with ψ-ionone and ionone is not observed when starting from citrylidene ethyl acetoacetate. The product obtained by Sehler[5]) by rearrangement of citrylidene ethyl acetoacetate with strong acids which he regarded to be a cyclic ester and termed α-ester, was no pure body, neither was Stötzner's[6]) α-ester pure. Both authors had not borne in mind that the primary condensation-product from equal molecules of citral and ethyl acetoacetate, during prolonged heating, and partially even on distilling, suffers a rearrangement.

By means of careful investigations, Knoevenagel established the difference of the original condensation-product from citral and ethyl acetoacetate (in whose preparation all heating was avoided) from the ester obtained by several hours' heating with exclusion of water. The primary ester was now termed α-ester, the one resulting from rearrangement by heat, β-ester. In the various reactions to which the α- and the β-derivatives were subjected, additional rearrangements took place; the bodies resulting hereby were termed by Knoevenagel α- and β-*iso* or -*pseudo* compounds.

α-Citrylidene acetoacetic ester, the primary condensation-product resulting from a mixture of equal molecules of citral and ethyl acetoacetate on addition of piperidine after prolonged standing in the cold, yields, on treatment according to Tiemann, no

[1]) *Journ. chem. Soc.* **113** (1918), 585. — [2]) *Liebig's Annalen* **221** (1883), 304. — [3]) *Journ. chem. Soc.* **107** (1915), 267. — [4]) *Journ. f. prakt. Chem.* II. **97** (1918), 288. — [5]) *Inaug.-dissert.*, Heidelberg 1897. — [6]) *Inaug.-dissert.*, Heidelberg 1900.

derivatives of the ionone series. The α-ester dissolves in aqueous sodium hydrogen sulphite on heating gently. This speaks in favour of the fact

$$(CH_3)_2C:CH\cdot CH_2\cdot CH_2\cdot C:CH\cdot CH:C\cdot CO\cdot CH_3$$
$$\qquad\qquad\qquad\qquad\quad CH_3 \qquad\quad COOC_2H_5$$

α-Citrylidene acetoacetic ester.

that in this ester a double-linking is vicinal to a carbonyl group. The ester, a light yellow, faintly smelling liquid, must be kept protected from light, otherwise a partial formation of the β-ester seems to take place.

α-Iso*citrylidene acetoacetic ester* is obtained from α-citrylidene ester by addition of HBr and re-abstraction by means of weak alkalies, or by rearrangement of the α-ester on treatment with strong acids. According to its probable constitution, this ester may be termed terpinolenyl acetoacetic ester, and Knoevenagel suggests two formulæ for this product. It is insoluble in acid sodium sulphite.

The *α-iso* ester as well as the α-ester are both difficult to saponify. The *α-iso* citrylidene acetoacetic acid, when recrystallised from alcohol, melts at 175° with evolution of CO_2. The re-esterification of the acid can be performed by treating the silver salt with ethyl iodide and yields the original *α-iso* ester.

*α-Iso*citrylidene acetoacetic acid (terpinolenyl acetoacetic acid), on heating, undergoes a splitting-off of CO_2 which characterises all the β-ketonic acids, whereby *α-iso* ionone, or terpinolenyl acetone, is formed. This ketone is a yellowish oil of a weak, terpene-like odour; b. p. 122° at 23 mm.; semicarbazone, m. p. 205° with decomposition.

From the *α-iso* acid, two acids are obtained by oxidation with $KMnO_4$, an acid $C_{14}H_{24}O_5$, m. p. 192°, and an acid $C_{12}H_{22}O_4$, m. p. 183.5°. The latter acid splits off water very readily with formation of two isomeric bodies $C_{12}H_{20}O_3$, m. p. 111° and 94°. The first-named one reacts with *p*-bromophenylhydrazine, forming a product of the m. p. 174°.

On oxidation of *α-iso*citrylidene acetoacetic ester with chromic acid, a body $C_{13}H_{18}O_4$ resulted which owing to its low m. p., 42°, could not be purified by recrystallisation; semicarbazone, m. p. 193°.

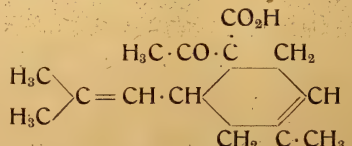
*α-Iso*ionone, on oxidation with chromic acid in glacial acetic acid solution, gave rise to a body $C_{12}H_{18}O_2$; b. p. 168 to 171° at 22.5 mm.

β-Citrylidene acetoacetic ester is obtained very readily on heating the dry α-citrylidene ester; it is insoluble in sodium hydrogen sulphite.

$$(CH_3)_2C:CH\cdot CH_2\cdot CH:C\cdot CH:CH\cdot CH\cdot CO\cdot CH_3$$
$$\qquad\qquad\qquad\qquad\quad CH_3 \qquad\quad COOC_2H_5$$

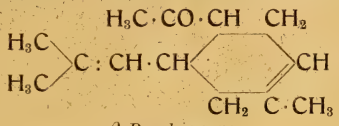
Probable formula of β-citrylidene acetoacetic ester.

On treatment with strong alkalies, the β-ester is converted into β-pseudo *citrylidene acetoacetic acid*. When esterified anew, this acid yields a new citrylidene acetoacetic ester, and for this reason the acid and its esters were termed *pseudo* compounds. In the formation of the ψ-acid from the β-ester, a cyclisation has evidently taken place. The ψ-acid melts at 138° wits copious evolution of CO_2. On esterification by means of alcohol and sulphuric acid, the acid passes over into *β-ψ-citrylidene acetoacetic ester*, m. p. 99 to 100°.



Probable formula of β-*pseudo*citrylidene acetoacetic acid.

The preceding formula of β-ψ-citrylidene acetoacetic acid is supported by the results of the oxidation by aqueous-alkaline permanganate solution. By action of six atoms of oxygen, a solid degradation-product was obtained, 3-methyl-2-butenyl pyruvic acid $(CH_3)_2C:CH\cdot CH_2\cdot CH_2\cdot CO\cdot COOH$, m. p. 192° with strong evolution of CO_2. When heated in the dry state, β-ψ-citrylidene acetoacetic acid yields *β-pseudo*ionone, a feebly-smelling oil of the b. p. 130° (23 mm.), insoluble in aqueous potassium hydrogen sulphite; semicarbazone, m. p. 152°.

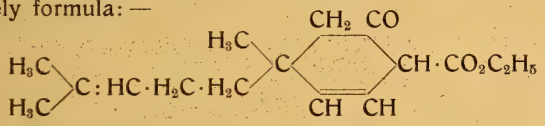


*β-Pseudo*ionone.

In the cold, β-citrylidene acetoacetic ester yields with HBr + glacial acetic acid a solid hydrobromide, m. p. 93 to 94°.

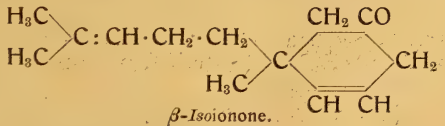
When heated with zinc chloride, the β-ester passes over, with evolution of CO_2, into the hydrocarbon $C_{13}H_{18}$, *β-ionene*, an oil of characteristic smell and the exceptionally low b. p. 63° (12 mm.). The well-studied hydrocarbons ionene and irene show the b. p. 106 to 107° (10 mm.) and 113 to 115° (9 mm.) respectively.

β-Citrylidene acetoacetic ester, in analogy with the α-isomeride, suffers, on treatment with, and re-abstraction of, hydrogen bromide (by means of sodium carbonate) a rearrangement and yields an isomeride, *β-iso*citrylidene acetoacetic ester of a somewhat lower boiling point, with the likely formula: —



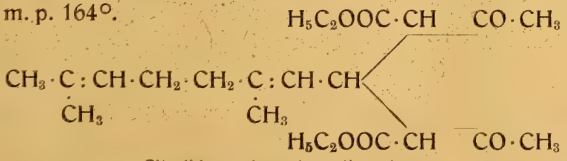
*β-Iso*citrylidene acetoacetic ester is a light yellow oil with a pleasant smell. Its hydrobromide is identical with the one resulting from β-citrylidene acetoacetic ester.

The free *β-isocitrylidene acetoacetic acid* melts at 153°; on oxidation with potassium permanganate in sodium carbonate solution small amounts of an acid melting at 160 to 165° are formed. When esterified, by treatment of the silver salt with ethyl iodide, the acid is retransformed into the original ester. On heating above the m. p., *β-iso* citrylidene acetoacetic acid gives rise to *β-isoionone*, an oil of terpenic smell, b. p. 113° (15 mm.); semicarbazone, m. p. 108°; *p*-bromophenylhydrazone, m. p. 150 to 152°.



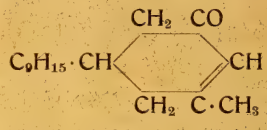
*β-Iso*ionone.

On condensing citral with two molecules of ethyl acetoacetate by means of organic bases, *citrylidene* bis-*acetoacetic ester*, a body belonging to the 1:5-diketones, is formed. This ester does not undergo the complicated isomerisations of the *mono*acetoacetate series dealt with above. For its preparation, two molecules of ethyl acetoacetate and one mol. of citral, with addition of piperidine, are allowed to stand for some time in a freezing mixture; m. p. 64°; oxime, m. p. 164°.



Citrylidene *bis*-acetoacetic ester.

Citrylidene *bis*-acetoacetic ester lends itself to various reactions. When boiled with alcoholic caustic potash it passes over into methyl-1-(dimethyl-2:6-heptadienyl)-3-*cyclo*hexenone-5, a limpid oil of the b. p. 197 to 198° (15 mm.). This ketone, on reduction with sodium and alcohol, passes over into methyl-1-(dimethyl-2:6-heptadienyl)-3-*cyclo*hexanol-5, a limpid, water-white oil boiling at 163 to 164° (11 mm.). Neither the alcohol nor the ketone gave solid addition-products with bromine. On oxidation with Beckmann's chromic acid mixture, the alcohol yields methyl-1-(dimethyl-2:6-heptadienyl)-3-*cyclo*hexanone-5 which after purification by means of the bisulphite compound boiled at 172° (15 mm.). With P_2O_5, methyl-1-(dimethyl-2:6-heptadienyl)-3-*cyclo*hexanol-5 formed the hydrocarbon methyl-1-(dimethyl-2:6-heptadienyl)-3-cyclohexene; b. p. 143 to 144° (15 mm.).



Methyl-1-(dimethyl-2:6-heptadienyl)-3-*cyclo*hexenone-5.

G. Romeo[1]) reports on the *hydrosulphonic derivatives of citral*. He deals with the well-known normal double compound with sodium hydrogen sulphite, the stable and the unstable dihydrosulphonates, the monohydrosulphonate, and furthermore with an unstable and a stable trihydrosulphonate. The unstable trihydrosulphonate, $C_{10}H_{19}O_{10}S_3Na_3$ results on shaking citral with a solution of sodium sulphite and bisulphite first at ordinary temperature, followed by gentle heating. It is an odourless, non-deliquescent mass, easily reducible to powder, very readily soluble in water with slight evolution of heat, somewhat soluble in methyl alcohol, and showing only slight opalescence on addition of barium chloride solution. On addition of potash solution, citral separates off, but not on addition of sodium carbonate solution. A small amount of the stable trihydrosulphonate is formed simultaneously with the unstable modification, a white, light, non-deliquescent powder, extremely soluble in water, but rather difficultly soluble in methyl alcohol. No citral is separated off on addition of potassium hydroxide.

On the *conversion of citral into geraniol* by means of yeast, *vide* p. 143 of this *Report*.

As to the *transformation of* d, l-*methyl ethyl acetic aldehyde into* l-*amyl alcohol*, compare p. 143 of this *Report*.

Re the *reduction of œnanthic aldehyde*, see p. 71 of this *Report*.

Concerning the *estimation of aromatic aldehydes* by means of *hydrazine*, *vide* p. 87 of this *Report*.

Ketones.

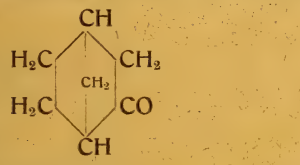
On the formation of ketonic semicarbazones. — It is a well-known fact that not all the ketones react with semicarbazide with equal velocity; in some cases, the interaction proceeds very rapidly, in others, extremely slowly. In general, aliphatic ketones and such aromatic ketones as contain the carbonyl group in the side-chain react readily.

Those of our readers who are interested in the relations between the course of the semicarbazone formation and the chemical structure of the ketones are referred

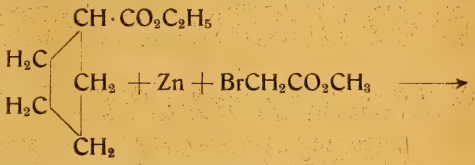
[1]) *Gazz. chim. ital.* **48** (1918), I. 45; *Chem. Zentralbl.* **1918**, II. 1027.

to a paper by A. Michael[1]), entitled, "The Relations between the chemical Structure of Carbonyl Derivatives and their Reactivities towards Salts of Semicarbazide". In this paper, which is unsuitable for short abstracting, a theory for these interactions is put forward. The ketones investigated and ranging within our scope of interest were: — methyl amyl ketone, methyl hexyl, -octyl, -nonyl ketones, ethyl amyl ketone, *cyclo*hexanone, and acetophenone. Additionally, the following aldehydes were investigated: — *Iso*valeric aldehyde, œnanthol, benzaldehyde, salicylaldehyde, anisic, and cinnamic aldehydes.

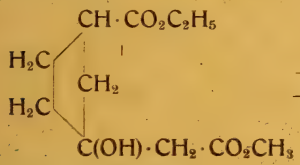
Nor-*camphor*. — The parent substance underlying all derivatives of the camphor series, *i. e., nor*-camphor (I)[2]) = bi*cyclo*(1.2.2)-heptanone-2, from which camphor, fenchone, camphenilone, and fenchocamphorone are derived, was hitherto unknown. A synthesis of this interesting body has now been published by S. V. Hintikka and G. Komppa[3]). After several unsuccessful attempts they resorted to Reformatzky's reaction and condensed



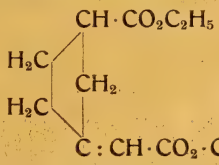
(I) *Nor*camphor.



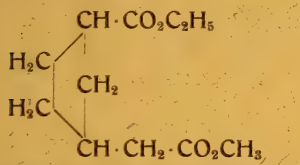
(II) Ethyl *cyclo*pentanone carboxylate.



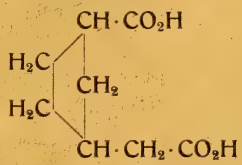
(III) Methyl ethyl hydroxy-homo-*nor*camphorate.



(IV) Methyl ethyl dehydrohomo-*nor*camphorate.



(V) Methyl ethyl homo-*nor*camphorate.



(VI) Homo-*nor*camphoric acid.

ethyl *cyclo*pentanone carboxylate (II) with methyl bromoacetate, when methyl ethyl hydroxyhomo*nor*camphorate (III) resulted. By abstracting water this ester yielded methyl ethyl dehydrohomo*nor*camphorate (IV) which on addition of hydrogen passed over readily into methyl ethyl homo*nor*camphorate (V). From this ester, there resulted, on saponification, homo*nor*camphoric acid (VI), the lead salt of which yielded, by dry distillation, the *nor*-camphor looked for.

For the preparation of ethyl hydroxy homo*nor*camphorate, ethyl 1:3-*cyclo*pentanone carboxylate and methyl bromo acetate were heated, in benzene solution, with zinc shavings. The ester (III) was a colourless oil which on heating with sodium hydrogen sulphate lost water with formation of methyl ethyl dehydrohomo*nor*camphorate (IV); b. p. 143 to 145° (13 mm.). This ester, on reduction with colloidal platinum or palladium, gave methyl ethyl homo*nor*camphorate (V); b. p. 135 to 141° (13 mm.). By saponification,

[1]) *Journ. Americ. chem. Soc.* **41** (1919), 393. — [2]) Concerning the nomenclature of the camphor derivatives, see G. Komppa, *Berl. Berichte* **42** (1909), 898. — [3]) *Annal. Acad. Scient Fenn.*, Series A. **10** (1919), No. 22.

the free acid (VI) was obtained; m. p. 137 to 137.5°; anilide, m. p. 195 to 198.5°. Lead homo*nor*camphorate, a crystalline precipitate, resulted on adding lead acetate to the solution of the ammonia salt of the acid. From a concentrated solution, the lead salt separates only after boiling and adding water in which it is comparatively easily soluble. On dry distillation of lead homo-*nor*camphorate in an atmosphere of CO_2, nor*camphor* (I) is formed; m. p. 93 to 94°; semicarbazone, m. p. 196.5 to 197.5°. *Nor*camphor is comparatively readily soluble in water and turns oily when in contact therewith; it is a very volatile body of intense, biting smell and burning taste. In case it possesses the same physiological effect on the heart and the respiration as ordinary camphor, and in case it could be made easier accessible, the authors are of opinion that the body may become important for therapeutic purposes[1]).

On the *phytochemical reduction of methylheptenone, vide* p. 140 of this *Report.*

Eucarvone. — As is generally known, eucarvoxime, on reduction with palladium and hydrogen, yields β-dihydroeucarvoxime, m. p. 123°, and the latter, on hydrolysis, β-dihydroeucarvone (I)[2]). The ketone, in glacial acetic acid solution, adds readily bromine with formation of a dibromide, m. p. 71 to 72°, to which the formula of a 1 : 7-dibromo-1 : 4 : 4-trimethyl*cyclo*heptanone-2 (II) is assigned, and on which Wallach[3]) brings new details. The body is isomeric with the bromide (III) (m. p. 68°), resulting on direct bromination of tetrahydroeucarvone. The bromide of the m. p. 71 to 72° reacts readily with caustic potash, yielding volatile products and an acid. Amongst the former, a halogen-free ketone predominates which resembles none of the ketones of the eucarvone series. Evidently, a far-reaching transposition has taken place. The ketone yields very readily a semicarbazone, m. p. 194 to 195°, from which either an open-chain formula, or a side-chain position of the carbonyl group may be inferred. With palladium and hydrogen it is converted into a saturated ketone; semicarbazone, m. p. 196 to 197°. The alkaline liquid contained an acid $C_{10}H_{16}O_2$, m. p. 104 to 105°; which on careful oxidising with permanganate passed over into an acid, m. p. 201 to 202°. Evidently the acid $C_{10}H_{16}O_2$ is identical with α-*cyclo*geranic acid (IV) (*iso*geranic acid) obtained by Tiemann and Semmler from citral. For reason of a direct comparison, Wallach prepared the latter acid which is easily accessible by abstracting water from citral oxime by means of acetic anhydride, by saponifying the resulting nitrile (purified by vacuum distillation) with alcoholic potash, and shaking the geranic acid thus obtained, for several hours and at ordinary temperature, with sulphuric acid of 65 to 70 per cent. The α-*cyclo*geranic acid resulting hereby melted an 104 to 105° and showed no depression of the m. p. when mixed with the acid from dihydroeucarvone dibromide of the same m. p. At the same time Wallach established the fact that α-*cyclo*geranic acid may be reduced to 1 : 3 : 3-trimethyl*cyclo*hexane-2-carboxylic acid by means of palladium and hydrogen; m. p. 82 to 83°. The formation of α-*cyclo*geranic acid from the dibromide (II) is easily explained when Wallach's formula for β-dihydroeucarvone is accepted. In this case, a rupture of the heptacyclic ring between the carbon atoms 1 and 7, followed by hydrolysis, would have to be assumed, which in its turn is followed by ring-closure, with elimination of hydrogen bromide or of water, and formation of the hexacyclic unsaturated acid, as is demonstrated by the formulæ given below.

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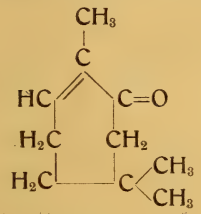
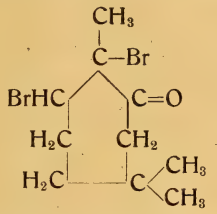
[1]) Compare D. R. P. 289950, Process of preparing solutions of *nor*camphor suitable for hypodermic injections; *Therap. Monatsh.* **30** (1916), 342. In the patent specification, the ready solubility of *nor*camphor in water is emphasised. — [2]) Wallach, *Liebig's Annalen* **403** (1914), 91; *Report* April **1914**, 143. — [3]) Wallach, *Liebig's Annalen* **418** (1919), 53.

The dibromide from β-dihydroeucarvone (II), on bromination in glacial acetic acid solution, with heating, is converted into a tribromide (V), m. p. 104 to 105°, which on shaking with a 2 per cent. potash solution yields an acid, m. p. about 170°. Strangely, the isomeric dibromide (III) from tetrahydroeucarvone adds no more bromine when treated under the same conditions.

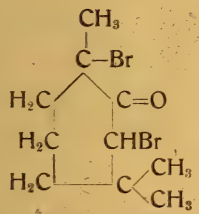
Furthermore, Wallach reports on the interaction of the dibromide $C_{10}H_{16}Br_2O$ (III), m. p. 68°, from tetrahydroeucarvone with caustic potash. Treatment with aqueous potash of this dibromide resulted in a saturated monobasic acid, m. p. 91.5 to 92.5°[1]) and in volatile products which Wallach now investigated closely. They form a mixture boiling principally between 35 and 75° and 93 to 95°, at 8 mm. The lower-boiling fractions boiled, under ordinary pressure, in the main at 138 to 140° and contained probably hydrocarbons owing to a secondary reaction. The higher fraction boiled, under ordinary pressure, irregularly up to 230°, showed bright yellow coloration and high density (0.988 at 20°). No characteristic products were obtainable from this



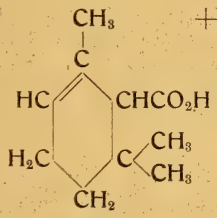
(I) β-Dihydroeucarvone.



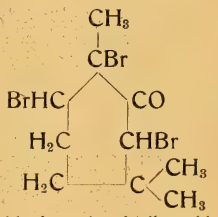
(II) Dibromide of m. p. 71 to 72° from β-dihydroeucarvone.



(III) Bromide of m. p. 68° from tetrahydroeucarvone.



(IV) α-*Cyclo*geranic acid.



(V) Probable formula of tribromide $C_{10}H_{15}Br_3O$ from β-dihydroeucarvone.

preparation. On reduction with palladium and hydrogen, the fraction added readily hydrogen and yielded a colourless liquid boiling principally between 223 and 225° ($d_{20°}$ 0.9690). It formed a semicarbazone, m. p. 212 to 213°, and an oxime, m. p. 55 to 56°. On oxidation with potassium permanganate two acids were formed, a volatile one smelling of *iso*butyric acid, and a non-volatile one which did not solidify. Possibly, it is here the question of a cyclic ketone with the carbonyl group in the lateral chain. In any case, the compound is not identical with monohydroxytetrahydroeucarvone[1]).

The volatile acid $C_{10}H_{16}O_2$ mentioned above, m. p. 91.5 to 92.5°, is isomeric with *α-cyclo*geranic acid. It is rather stable towards potassium permanganate, but nevertheless can be oxidised in alkaline solution resulting in a mixture from which three acids could he isolated:— an acid $C_{10}H_{16}O_3$ (m. p. 159 to 160°), an acid $C_{10}H_{14}O_3$ (m. p. 187°), and an acid, m. p. 90 to 91°.

Wallach then deals with the interaction of dibromotetrahydroeucarvone with sodium methoxide, which we referred to in our *Report* of **1918**, 137. The result is a neutral

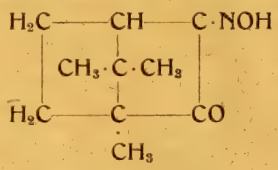
[1]) Wallach, *Liebig's Annalen* **414** (1918), 373; *Report* **1918**, 137.

liquid $C_{10}H_{16}O_2$ isomeric with the aforesaid, acid $C_{10}H_{16}O_2$ and smelling of cloves, in addition to a small amount of the acid $C_{10}H_{16}O_2$ of the m. p. 91 to 92°. The oil smelling of cloves boiled at 90° (7 mm.); $n_{D19°}$ 1.4693. It is remarkably stable towards potassium permanganate and yields a bromide which on treatment with diluted caustic potash solution is converted into a solid acid apparently identical with the acid resulting from the acid $C_{10}H_{16}O_2$ on oxidation. On standing the clove-like smelling oil was rearranged to a aliphatic ketone smelling of amylacetate, the semicarbazone of which melted at 188 to 189°.

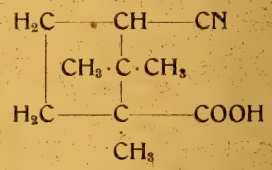
With the simplest dibrominated *cyclo*heptanone, dibromosuberone, the interaction with caustic potash passes off differently from the reaction with the hexacyclic ketones. Dibromosuberone, on shaking with dilute potash at 70°, dissolves very quickly yielding a neutral product (semicarbazone, m. p. 190 to 191°) and an acid (possibly tetrahydrobenzoic acid), both volatile with steam.

Carvone camphor. — Sernagiotto[1]) gives further details about this strange ketone obtained by Ciamician and Silber[2]) on exposing carvone to the action of light. Earlier investigations by Sernagiotto were published at different times[3]). The oxime of carvone camphor was treated with reagents which generally cause isomerisation of oximes. On heating with 20 per cent. sulphuric acid up to 100°, *iso*-carvone camphor was obtained, characterised by its semicarbazone. This ketone has been described in an earlier publication. Action of phosphorus pentachloride on the oxime dissolved in dry chloroform resulted in the formation of 2-monochlorocymene and of a body $C_{10}H_{13}ON$ of unknown constitution.

Camphor. — According to statements by Kötz and Wunstorf[4]), *iso*nitrosocamphor, when heated up to 240°, is decomposed into camphoric anhydride and dimethylheptenic nitrile, which statement, according to Sernagiotto[5]), is in disagreement with the fact that benzil α-oxime, with the same grouping $:C\cdot CO\cdot C(NOH)\cdot C:$, yields



(I) *Iso*nitrosocamphor.



(II) Camphoric acid α-nitrile.

benzoic acid and benzonitrile on heating. Sernagiotto found that in fact *iso*nitrosocamphor (I) behaves exactly like benzil α-oxime; as it passes over, at 206 to 207°, into camphoric acid α-nitrile (II); needles, from water, m.p. 151°. In addition, a compound $C_{10}H_{16}O$, b.p. 198 to 200°, is formed, volatile with steam and showing ketonic or aldehydic properties; its constitution has not yet been established.

Fenchone. — As to the cryoscopic behaviour of this ketone, *vide* p. 102 of this *Report*.

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[1]) *Gazz. chim. ital.* **48** (1918), I. 52; *Chem. Zentralbl.* **1918**, II. 1027. — [2]) *Berl. Berichte* **41** (1908), 1928; *Report* November **1908**, 159. — [3]) *Atti R. Accad. dei Lincei* (5) **23** (1914), I. 70; *Chem. Zentralbl.* **1914**, II. 1398. — *Gazz. chim. ital.* **47** (1917), I. 153; *Journ. Soc. chem. Industry* **36** (1917), 614. — Comp. *Reports* April **1915**, 99; **1918**, 137. — [4]) *Journ. f. prakt. Chem.* II. **88** (1913), 519; *Report* April **1914**, 148. — [5]) *Atti R. Accad. dei Lincei* (5) **26** (1917), II. 221; *Chem. Zentralblatt* **1918**, II. 276.

Ketocineole. — Some years ago, G. Cusmano and A. Linari[1]) described a ketone $C_{10}H_{16}O_2$ (ketocineole) showing a feeble smell of cineole. Recently, Cusmano[2]) has observed that this ketone, in the same manner as camphor, accelerates catalytically the formation of sulphuryl chloride from sulphur dioxide and chlorine. The same acceleration, discovered by Schulze[3]) and utilised on factory scale, was found to take place also with *cyclo*hexanone, menthone, and tetrahydrocarvone. On the other hand, the reaction does not pass off in presence of α-monobromo camphor, camphor sulphonic acid, or camphor quinone. Monochloro- or -bromoketocineole are likewise without effect, the latter, however, may be realised by introducing a positive radical into the molecule, *e. g.* by converting the sulphonic acid into the amide, or the quinone into its oxime. Camphor oxime and *per*nitroso camphor oxime act equally as accelerators. All the compounds mentioned dissolve in liquid sulphur dioxide. On distilling off the sulphuryl dichloride, either the catalyst or its reaction-product is recovered; with ketocineole this is the identical chlorinated product as is obtained when chlorinating in light petroleum solution. This compound, however, is not formed during the formation of sulphuryl chloride, but only on the distilling off the latter, hence by action of the boiling sulphuryl chloride.

Menthone. — On page 129 of our *Report* for 1918, we brought an abstract of a preliminary publication[4]) of Wallach on the conversion of menthone into pulegenone. Recently, the same author[5]) published a second paper on this reaction, from which we gather some details in order to supplement our former abstract. We then mentioned the fact that in Wallach's opinion Cusmano's formula for the monobromide of buchu camphor (m.p. 77 to 78°; according to Cusmano, 85°) is incorrect. Cusmano ascribes formula I to the bromide and takes for granted that the formula for buchu camphor is the one put forward by Semmler (II). Cusmano bases his view on the fact that he found the bromide, on treatment with alkali, to pass over into hydroxythymoquinone, and infers therefrom that in this reaction bromine is interchanged for hydroxyl with simultaneous oxidation, the hydroaromatic compound formed primarily being converted into an aromatic one. Wallach was able to prove that the reaction proceeds differently, by succeeding in abstracting hydrogen bromide from the bromide on heating with pyridine, with formation of hydroxythymoquinone. Since this reaction passes off without the presence of water, it may be concluded that the formation of hydroxythymoquinone from the monobromide, as primary reaction-product, is not effected by interchangement of bromine for hydroxyl, but that, for the first, hydrogen bromide is split off. Hence, the conclusion leading to the assumption of position 5 for the bromine atom of the monobromide was disproved. Wallach takes it for far more probable that on brominating the hydroxyketone the tertiary H-atom in position 4 is substituted by bromine, thus resulting in formula III for the monobromide. On the other hand, it must be admitted that rearrangements may take place in the reaction, so that possibly a bromide of formula I is formed.

The formation of the other monobromide m.p. 100 to 101° (also mentioned in our former abstract) seems to depend largely on the temperature of the bromination, as to which Wallach gives exact details. It would lead us too far to reproduce them in full. On further bromination of this monobromide, in glacial acetic acid solution,

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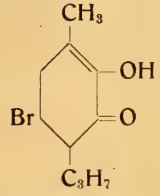
[1]) *Gazz. chim. ital.* **42** (1912), I. 1; *Chem. Zentralbl.* **1912**, I. 1021; *Report* October **1912**, 167. — [2]) *Atti R. Accad. dei Lincei* (5) **27**, II. (1918), 201; *Chem. Zentralbl.* **1919**, III. 93. — [3]) *Journ. f. prakt. Chem.* II. **24** (1881), 168. — [4]) *Nachr. K. Ges. Wiss., Göttingen* **1917**, meeting of Oct. 26. — [5]) *Liebig's Annalen* **418** (1919), 36.

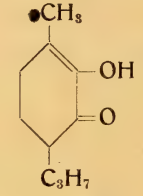
a colourless compound of the m.p. 162° is formed, probably a dibromide. The interesting dibromide $C_{10}H_{14}Br_2O_2$ (IV), m.p. 44 to 45°, is arrived at by different methods, as we mentioned formerly; the original paper gives exact details how this is perfected.

The estimation of the bromine in the dibromide may be carried out according to Carius, but equally well the dibromide may be boiled, in a small flask under a reflux condenser, with freshly prepared sodium methoxide, until the decomposition is completed. The alcohol is driven off and in the residue, after addition of nitric acid, the bromine is thrown down by silver nitrate[1]). On treatment with zinc dust in glacial acetic acid solution, the dibromide passes over into the primary compound $C_{10}H_{16}O_2$.

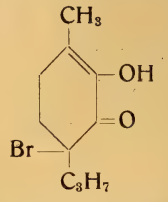
The acid $C_{10}H_{20}O_6$ (V), m.p. 88 to 89°, formed on interaction of the dibromide with alkali yields, on dry distillation, the ketone $C_9H_{14}O$ mentioned before, the identity of



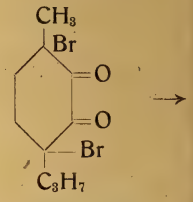
(I) Monobromide from buchu camphor acc. to Cusmano.



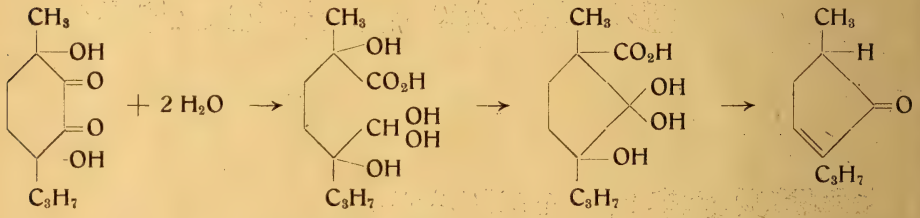
(II) Buchu camphor acc. to Semmler.



(III) Probable formula of monobromide acc. to Wallach.



(IV) Probable formula of dibromide $C_{10}H_{14}Br_2O_2$ of m.p. 44°.



(V) Probable formula of acid $C_{10}H_{20}O_6$.

(VI) Pulegenone.

which with pulegenone (VI) may be assumed. The course of this reaction is made clear from the above formulæ.

The character of the acid $C_{10}H_{20}O_6$ as an aldehydo acid seems to be disproved by the fact that the acid does not manifest reducing qualities to such an extent as might be expected from a body of the formula V.

Wallach then undertook a series of test experiments in order to decide whether the reaction discovered in the interaction of the bromine derivatives of the compound $C_{10}H_{16}O_2$ from menthone might be applied to analogous compounds of the series $C_nH_{2n-4}O_2$. In fact, the author succeeded in obtaining from the body $C_7H_{10}O_2$ (m.p. 62 to 63°, from dibrominated 1:2-methyl*cyclo*hexanone)[2]) different bromides, according to the method of brominating. Excess of bromine, when acting on the compound $C_7H_{10}O_2$ in ethereal solution, yielded a tribromide, m.p. 115 to 116°, from which on reduction with zinc and glacial acetic acid the original body $C_7H_{10}O_2$ was recovered. On treatment with but 1 molecule of bromine, a bromide of the m.p. 180° results.

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[1]) Comp. Wallach, *Berl. Berichte* **14** (1881), 753. — [2]) *Liebig's Annalen* **414** (1918), 314; *Report* **1918**, 127.

It is soluble in alkalies, turns dark when exposed to the air owing to absorption of oxygen, and yields after acidulating a yellow compound, volatile with steam, possibly a hydroxyquinone. Thence it seems possible to generalise the newly-described reactions.

On the *inversion of menthone*, we refer to p. 98 of this *Report*.

A short time ago, H. Rupe, in community with M. Iselin[1]) and E. Burckhardt[2]), described numerous *derivatives of methylene camphor*. The optical investigation of these highly rotating bodies led to the discovery of various new and interesting facts. In this connection, the authors were much interested in the preparation of an unsaturated ketonic derivative of camphor starting from a derivative of methylene camphor. The results of this extensive investigation have now been published by H. Rupe, M. Werder, and K. Tagaki[3]).

The authors started from hydroxymethylene camphor (I) which they converted, by treatment with dry hydrocyanic acid and with finely powdered potassium cyanide, into the nitrile of camphorylidene-3-acetic acid (II), m. p. 119 to 120°. The saponification of the nitrile was performed with a mixture of hydrochloric and glacial acetic acid. Camphorylidene acetic acid (III)[4]) forms lemon-yellow prisms, m. p. 99.5 to 101°; b. p. 185.5 to 187° (11.5 mm.); $[\alpha]_D$ 182.29°[5]) in a 10 per cent. benzene solution. The diluted solution of the alkali salts is colourless.

The chloride of camphorylidene acetic acid (IV), m. p. 34 to 35°, b. p. 140 to 141° (13 mm.), is readily formed on treatment of the free acid with thionyl chloride.

With hydrogen bromide in glacial acetic acid, camphorylidene acetic acid yields the hydrobromide (V), m. p. 153 to 154°. Evidently, the addition of HBr is a reversible reaction; in the cold, HBr is added, and at 100° it is split off again with quantitative formation of camphorylidene acetic acid. The addition of bromine to the acid does not pass off in the normal manner, and the constitution of the bromo derivative (m. p. 73 to 75°) could not yet be ascertained. The ethyl ester boils at 149.5 to 150° (12 mm.); $[\alpha]_D$ 170.10°[6]) (undiluted); 160.39°[6]) in a 10 per cent. benzene solution.

Reduction of camphorylidene acetic acid with sodium amalgam or better with hydrogen in presence of nickel leads to camphoryl-3-acetic acid (methyl camphor carboxylic acid, VI); m. p. 83 to 84°; b. p. 191.5 to 192.5° (12 mm.); $[\alpha]_D$ 38.06°[6]) in a 10 per cent. benzene solution; ethyl ester, b. p. 154 to 155° (10 mm.); $[\alpha]_D$ 67.53° undiluted); 37.18°[6]) in a 10 per cent. benzene solution.

When trying to reduce the chloride of camphorylidene acetic acid with zinc and acetic acid, a strange reaction took place, *i. e.*, formation of a mixed anhydride of acetic and camphorylidene acetic acids (VII); m. p. 118 to 120°. The constitution of this compound could be elucidated by quantitative degradation to both acids.

The authors then treated camphorylidene acetic chloride (IV) with diethyl sodiomalonate and obtained a pure compound formed by condensation of two molecules of the chloride with one molecule of diethyl sodiomalonate:— the diethyl ester of di-(camphorylidene-3-acetyl)malonate ([dimethylene camphor carbonyl]-malonate) (VIII); m. p. 90 to 91°.

They further succeeded, with some difficulties, to saponify this high-molecular body to camphorylidene-3-acetone (IX) and camphorylidene-3-acetic acid (III), by boiling with

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[1]) *Berl. Berichte* **49** (1916), 25; *Report* **1916**, 123. — [2]) *Berl. Berichte* **49** (1916), 2547; *Report* **1917**, 155. — [3]) *Helvet. chim. acta* **1** (1918), 309. — [4]) Bishop, Claisen, and Sinclair, *Liebig's Annalen* **281** (1894), 387. — [5]) It is not stated whether the acid is dextro- or lævorotatory. — [6]) The direction of the rotation is not stated.

sulphuric and glacial acetic acids. The ketone is a heavy liquid with a faint aromatic smell and intense, bright yellow colour; b. p. 137 to 138° (10 mm.); $d_{4^\circ}^{20^\circ}$ 1.0327; $[\alpha]_D$ 208.81°[1]) (undiluted); 186.64° in a 10 per cent. benzene solution. The benzylidene derivative (X) presents itself in shape of bright yellow needles m. p. 94 to 95°; $[\alpha]_D$ 206.65°[1]) in a 10 per cent. benzene solution; *p*-nitrobenzylidene camphorylidene-3-acetone (XI), (from *p*-nitrobenzaldehyde and the ketone) forms small lemon-yellow crystals, m. p. 150 to 151°. The oxime of camphorylidene acetone is colourless, m. p. 142 to 143°; phenylhydrazone, orange-yellow needles, m. p. 145 to 146°; hydrazine derivative (XII), yellow needles, m. p. 112 to 113°; semicarbazone, white crystals, m. p. 223 to 224°.

Camphorylidene acetone dissolves in sodium hydrogen sulphite solution, forming a viscid, foaming, saponaceous liquid, from which on addition of water the major part of the ketone is thrown down.

The semicarbazone of camphorylidene acetone (XIV) was remarkable for its stability and could by no means be split up into semicarbazide and ketone, whereas the semicarbazone of the camphorylacetone (described below) is split up already on boiling with aqueous oxalic acid solution. In the author's opinion, the semicarbazone of camphorylidene acetone is doubtless a heterocyclic compound in which the double linking takes part, in analogy with the compound formed from semicarbazide and mesityloxide (XIII)[2]), since the constitution of this body is closely related to that of camphorylidene acetone. Probably, the constitution as expressed per formula (XIV) may be ascribed to the semicarbazone.

On decomposing diethyl dicamphorylidene acetyl malonate (VIII) with boiling alcohol and sulphuric acid a yellow body is formed as by-product, possibly a condensation-product of two molecules of camphorylidene acetone with elimination of one molecule of water.

By starting from camphoryl acetic acid (VI) it was intended to prepare the hydrogenated ketone, camphoryl-3-acetone (XV) in the same manner as the unsaturated ketone from the unsaturated acid. However, the interaction of the acid chloride with diethyl sodiomalonate proceeded but very slowly; on the other hand, camphorylidene acetone could be hydrogenated direct by means of hydrogen in presence of nickel, a reaction in which the keto-group was partly reduced. Camphoryl-3-acetone is a strongly refractive oil with a very bitter taste; b. p. 148.5 to 149° (12 mm.); $d_{4^\circ}^{20^\circ}$ 1.0213; $[\alpha]_D$ 49.25°[3]) (undiluted); 60.73° in a 10 per cent. benzene solution. It is far more unstable than camphorylidene acetone. Semicarbazone, m. p. 203 to 204°; benzal camphoryl-3-acetone, m. p. 75 to 76°; $[\alpha]_D$ 47.37°[3]) in a 10 per cent. benzene solution.

After many unsuccessful experiments, the authors succeeded in preparing a triketonic derivative of camphor by acting with sodium ethoxide on a mixture of ethyl camphoryl acetate and acetophenone, the yield, however, being but very poor. The resulting camphoryl-3-acetylacetophenone (XVI) may be purified by means of the copper salt; m. p. 59 to 61°; $[\alpha]_D$ 62.52°[3]) in a 10 per cent. benzene solution.

Finally, the authors draw attention to the fact that in all the reactions into which the lateral ketonic group of these newly prepared ketones enter, the ketonic group proper of the camphor nucleus remains unattacked, thus proving anew how inert this keto-group behaves.

As to the polarimetric investigation of the bodies described in this paper, the authors have compiled the results in tabular form, and we refer to the original paper

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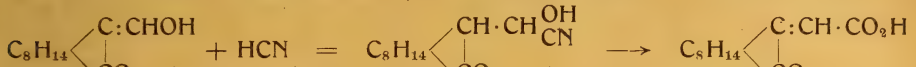
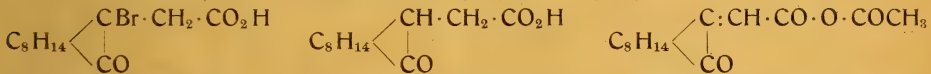
[1]) Direction of rotation not stated. — [2]) Compare *i. a.* Rupe and Kessler, *Berl. Berichte* **42** (1910), 4503. — [3]) Direction of the rotation is not stated.

for their study. Also in this investigation, it was proved more and more, in the authors' opinion, that in judging the relations between the rotatory power and the chemical constitution the course of the rotatory dispersion curve, compared with the curve of a substance of the same class, but with normal dispersion, is alone authoritative. Yet it is all the more striking that the benzylidene derivative shows a fully regular curve with the wave-length characteristic of the methylene camphor derivatives. Rupe and

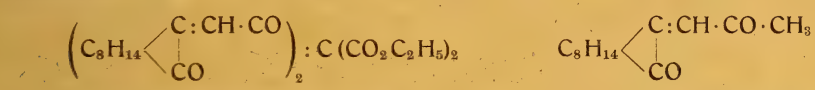


(I) Hydroxymethylene-camphor. (II) Nitrile of camphorylidene acetic acid. (III) Camphorylidene-3-acetic acid (Methylenecamphor carboxylic acid).

(IV) Camphorylidene-3-acetic chloride. Diethyl sodiomalorate. ⟶ VIII

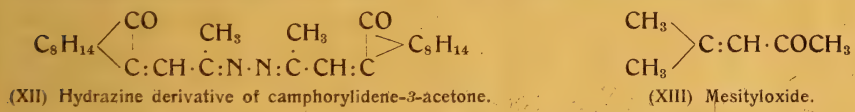


(V) Hydrobromide of camphorylidene acetic acid. (VI) Camphoryl-3-acetic acid (Methylcamphor carboxylic acid). (VII) Mixed anhydride of acetic and of camphoryl-3-acetic acids.

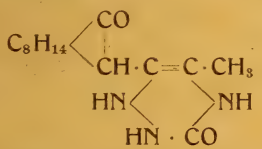


(VIII) Di-(camphorylidene-3-acetyl)malonic ester. (IX) Camphorylidene-3-acetone.

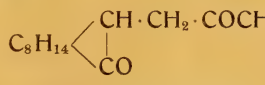
(X) Benzylidenecamphorylidene-3-acetone. (XI) *p*-Nitrobenzylidenecamphorylidene-3-acetone.



(XII) Hydrazine derivative of camphorylidene-3-acetone. (XIII) Mesityloxide.



(XIV) Possible formula of the compound from camphorylidene acetone and semicarbazide.



(XV) Camphoryl-3-aceton.

(XVI) Camphoryl-3-acetylacetophenone.

Wild[1]) have shown in a previous publication that on conversion of a ketone into its benzylidene compound the rotatory power is influenced but scarcely, because the C_6H_5CH: group, otherwise very active, is too far distant from the asymmetric carbon atom; yet a rotation amounting at least to that of the ketone might have been expected. The authors explain this fact provisionally by assuming that these unsaturated ketones are influenced strongly by the solvents. The hydrogenated compounds show all a decidedly lower rotatory power than the corresponding unsaturated ones.

[1]) *Liebig's Annalen* **414** (1917), 111.

Higher homologues of camphor. — Some years ago, A. Haller, in community with E. Bauer[1]), described the preparation of mono- and di-methylcamphor by treatment of sodiocamphor (from camphor and sodamide) with methyl iodide. Later on, in community with J. Louvrier[2]), he obtained various alkyl derivatives of camphor, and recently he reported, with E. Bauer[3]), on the preparation of mono- and dimethylcamphor, dimethyl campholic amide and dimethyl campholic acid. In a historical synopsis on the preparation of the alkyl camphors the various mistakes are dealt with which the former authors had committed when working on these camphor derivatives, and then a description is given how the different alkyl camphors and their derivatives were obtained.

In a flask with reflux condenser a mixture of 152 g. camphor, 500 g. dry ether or benzene, and 40 g. finely-powdered sodamide is introduced. Ammonia is evolved in the cold, and the mixture is heated for 5 hours on a water-bath. Methyl iodide (2/3 molecule), dissolved in ether or benzene is then added drop by drop. After 2 to 3 hours' heating the remainder of the methyl iodide is added, the heating is continued for 1/2 hour and the mixture allowed to cool down. The cold reaction-mixture is poured into water whereby sodium iodide and the hydriodides of methylated amines are dissolved; the supernatant liquid is drawn off, washed and distilled in order to drive off the solvent. The residue is distilled *in vacuo*; b. p. 95 to 110° (11 mm.), the distillate is a mixture of camphor, *mono-* and *dimethylcamphor* which is methylated anew. The final product, of the same b. p., contains no more camphor and is a mixture of mono- and dimethylcamphor which may be separated by oximation, since monomethylcamphor only yields an oxime. For this purpose, the mixture is heated, in twice its volume of alcohol, with zinc + hydroxylamine chlorides for three days. *Monomethylcamphoroxime* (V) boils at 134 to 135° (11 mm.); dimethylcamphor (I) at 106° (11 mm.); $d_{4^\circ}^{25^\circ}$ 0.94708; $[\alpha]_{D25^\circ}$ + 97° 50′; n_D 1.47187. The latter ketone is likewise stable towards all the other reagents for ketones. In alcoholic solotion, it is reduced by sodium to d-*dimethylcamphol* (dimethylborneol) (II), a product smelling of borneol and consisting evidently of a mixture of α- and β-dimethylcamphol. The α-isomeride which separates first from the mixture melts at 56 to 57°; $[\alpha]_D$ + 55° 4′ (0.2095 g. in 10 cc. alcohol); $[\alpha]_D$ + 60° 4′ (0.1482 g. in 10 cc. benzene). The β-dimethylcamphol remained liquid and was naturally not chemically pure. By action of sodium amide, in benzene solution, on dimethylcamphor, *dimethylcampholic amide* (III) results, a body of extreme solubility in organic solvents; m. p. 72 to 73°; b. p. 179 to 180° (14 mm.). When treating the amide with sodium nitrite, *dimethylcampholic acid* (IV) is obtained; m. p. 73 to 74°.

α-*Monomethylcamphoroxime* (V) melts at 60°; b. p. 134 to 135° (11 mm.); $[\alpha]_D$ + 23.15° (0.488 g. in 10 cc. absolute alcohol). Since Glover[4]) quotes different properties for this oxime, the authors converted the oxime into the *carbanilide* (phenylurethane). This body (VI) was obtained in an inactive as well as an active form ($[\alpha]_D$ + 24.8° [0.4275 g. in 10 cc. absolute alcohol]) which both method about 112 to 113°; the mixture showed but slight depression of the m. p. Both isomerides differed from each other by their solubility. The authors conclude from the course of the action of phenyl*iso*cyanate on α-monomethylcamphor oxime that the latter was free from camphor oxime, the presence of which might have explained the variations from Glover's statements. α-Methylcamphoroxime prepared differently melted likewise at 113°.

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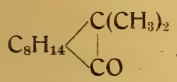
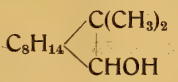
[1]) *Compt. rend.* **148** (1909), 1643; *Report* October **1909**, 199. — [2]) *Ibidem* **158** (1914), 754; *Report* April **1915**, 97. — [3]) *Annal. de Chim.* IX. **8** (1917), 117. — [4]) *Journ. chem. Soc.* **113** (1908), 1285.

By dehydration of α-methylcamphoroxime, the authors obtained *α-methylcampholenic nitrile*, described previously by Glover; b. p. 105 to 106° (16 mm.); $[\alpha]_D + 53.3°$ (0.464 g. in 10 cc. absolute alcohol). It is a colourless liquid with a very penetrating, rather pleasant smell. When heated with caustic alcoholic potash it is converted into α-methylcampholenic amide; m. p. 80 to 82° or 91 to 92° according to its crystallising with or without water. The amide is optically inactive; evidently a rearrangement has taken place by the action of alcoholic potash. The same rearrangement appears to pass off when the nitrile is saponified with dilute sulphuric acid.

Furthermore, Haller, in community with J. Louvrier[1]), reports on the preparation and investigation of various monoalkyl und dialkyl camphors and derivatives therefrom.

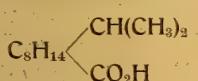


(I) Dimethylcamphor.

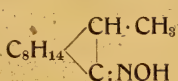


(II) Dimethylcamphol (Dimethylborneol).

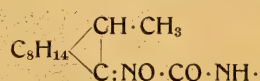
(III) Dimethylcampholic amide[2]).



(IV) Dimethylcampholic acid[2]).



(V) α-Monomethylcamphoroxime.



(VI) α-Methylcamphoroxime carbanilide (-phenylurethane)[2]).

Diethylcampholic amide, obtained by heating diethylcamphor with sodium amide; m. p. 75°; b. p. 185° (12 mm.); $[\alpha]_{D18°} + 76° 15'$ (0.1530 g. in 10 cc. alcoholic solution); *diethylcampholic acid*, from the amide with concentrated sulphuric acid and sodium nitrite; m. p. 78°; b. p. 157° at 20 mm.; $[\alpha]_{D15°} + 60° 59'$ (0.5137 g. in 10 cc. alcohol); *methylethylcampholic amide*, obtained from methylethylcamphor in the same manner; m. p. 60°; b. p. 180° at 14 mm.; $[\alpha]_{D15°} + 75° 42'$ (0.8236 g. in 10 ccm. alcohol); *methylethylcampholic acid*, m. p. 74°; $[\alpha]_{D15°} + 57° 10'$ (0.0991 g. in 10 cc. alcohol); *allylcamphor*, prepared from camphor, sodium amide, and allyl iodide; b. p. 118° at 12 mm.: $d_{0°}^{0°}$ 0.969; $[\alpha]_{D14°} + 78° 51'$ (0.6509 g. in 10 cc. alcohol); on reduction with sodium and alcohol it yields *allylborneol*, p. b. 119° at 14 mm.; $[\alpha]_{D16°} + 19° 23'$ (0.8429 g. in 10 cc. alcohol); phenylurethane, m. p. 64°. *Diallylcamphor* results on treating monoallylcamphor with sodium amide and allyl iodide; b. p. 155° at 16 mm.; $d_{0°}^{0°}$ 0,982; $[\alpha]_{D17°} + 148°$ (0.5427 g. in 10 cc. alcohol); by reduction with alcohol and sodium it yields *diallylborneol*, m. p. 47°; $[\alpha]_{D18°} + 77° 51'$ (0.3425 g. in 10 cc. alcohol); *dibenzylcampholic amide*, from dibenzylcamphor in the usual manner; m. p. 121°; b. p. 300° at 12 mm.; $[\alpha]_{D19°} + 33° 7'$ (0.2707 g. in 10 cc. alcohol). *Ethyl benzylcampholic amide*, from ethyl benzylcamphor, m. p. 181°; b. p. 230 to 240° (12 mm.).

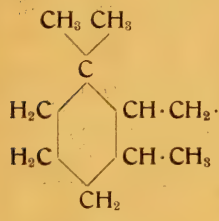
From ethylcamphoroxime were obtained:— the phenylurethane, m. p. 146°, and ethyl-α-campholenic nitrile (by heating the oxime with concentrated hydrochloric acid, or the ethylcamphoroxime carbanilide up to 130° in a vacuum); b. p. 110° (11 mm.); $d_{0°}^{0°}$ 0.903; $[\alpha]_{D13°} + 70° 33'$ (1.0489 g. in 10 cc. alcohol). On saponification it yields *ethyl-β-campholenic amide*, m. p. 62°. *Ethyl-β-campholenic acid*:— m. p. 36°; b. p. 157° (20 mm.). Allylcamphor yields *allylcamphoroxime*, b. p. 158° (16 mm.); $[\alpha]_{D14°} + 58° 10$ (0.2521 g. in 10 per cent. alcohol); phenylurethane, m. p. 160°; from which on treatment with acetyl chloride *allyl-α-campholenic nitrile* results; b. p. 130° (11 mm.); $d_{0°}^{0°}$ 0.934; $[\alpha]_{D14°} + 28° 40'$ (2.1044 g. in 10 cc. alcohol). With sodium ethoxide and water it passes over into *allyl-β-campholenic amide*, m. p. 97°, and *allyl-β-campholenic acid*, m. p. 49°; b. p. 156° (16 mm.). Propylcamphoroxime, $[\alpha]_{D15°} + 54° 50'$ (0.808 g. in 10 cc. alcohol),

[1]) *Annal. de Chim.* IX. 9 (1918), 189. — [2]) The formulæ of the original paper are incorrect.

yields on heating with hydrochloric acid *propyl-α-campholenic nitrile*; b. p. 124° (11 mm.); d_{00}^{00} 0.907; $[\alpha]_{D16°}$ + 46° 31′ (2.2564 g. in 10 cc. alcohol). *Propyl-β-campholenic amide* boils at 173° (12 mm.), *propyl-β-campholenic acid* at 160° (12 mm.). Benzylcamphoroxime yields on treatment with concentrated hydrochloric acid *benzyl-α-campholenic nitrile*, b. p. 195° at 14 mm.; $[\alpha]_{D17°}$ + 54° 23′ (1.5565 g. in 10 cc. alcohol); and with acetyl chloride a *nitrile*, $[\alpha]_{D17°}$ + 44° 24′ (1.5388 g. in 10 cc. alcohol). Both nitriles yield the same *benzyl-β-campholenic amide*, b. p. 197° at 12 mm. *Benzyl-β-campholenic acid* melts at 68°; b. p. 204° (12 mm.).

Irone. — Basing on his investigations on the relations between the ionones and irone, L. Ruzicka[1]) concludes that α- and β-ionone are not alone structurally isomeric with irone, but also stereoisomeric, *i. e.*, in addition to a different position of the cyclic double linking, *cis-trans*-isomerism also comes into consideration. It appears that for irone *trans*-position, and for the ionones *cis*-position of the substituting groups may be assumed.

Since Ruzicka was unsuccessful in proving, beyond doubt, the constitution of irone by means of ozonisation he made use of the catalytic reduction method by metals of the platinum group at ordinary temperature. He obtained hereby tetrahydroirone, thus proving that actually two double-linkings are present in irone, as might be deduced from the molecular refraction. However, the reduction-product is not identical with tetrahydroionone obtained by Skita[2]) from α- and β-ionone, as might have been expected from the current formulæ of irone and of α- and β-ionone, but differs therefore by its optical activity (dextrorotation, like irone itself), its higher specific gravity, and its boiling-point (by about 14° higher). From these different physical properties, Ruzicka infers *cis-trans*-isomerism between the ionones and irone.



Tetrahydroirone.

Tetrahydroirone, $C_{13}H_{24}O$, is an oil with a cedar-like odour; b. p. 143 to 145° (13 mm.); tetrahydroionone boils at 129° (13 mm.). The corresponding semicarbazones were likewise prepared by the author; they melt at 202 to 203°, and 183 to 184° respectively.

Furthermore, Ruzicka endeavoured to prove, by way of experiment, the structural identity of the tetrahydro compounds of irone and of both ionones, but was unable to solve the question either by experiments leading to mutual transformation by heating with hydrochloric acid or with alkali up to higher temperatures, or by degradation down to lower *"Abbau"* products. For the latter purpose, he prepared tetrahydroironic acid, $C_{12}H_{22}O_2$, by oxidation with sodium hypobromite at elevated temperature (b. p. 185° to 190° [15 mm.]; m. p. about 80°), and oxidised the acid furtheron with potassium permangate. Tetrahydroiononic acid presented itself as oil of the b. p. 173 to 178° (12 mm.). In both cases, no characteristic cleavage products were obtained besides oxalic acid.

Contrary to Skita's observations, only the tetrahydro compound was formed on reducing the ionones with colloidal palladium, but when working with platinum black according to Willstätter, hexahydroionone was formed additionally, for which Ruzicka prefers the term "tetrahydroionol". With Kelber's nickel catalyst[3]), a dihydroionol $C_{13}H_{22}O$, b. p. 135 to 140° (14 mm.) resulted, which is oxidised to a dihydroionone by means of chromic acid in glacial acetic acid; b. p. 130 to 132° (14 mm.); semicarbazone, m. p. 166 to 168°. Hence it appears that with the nickel catalyst, α-ionone suffers a reduction of the ketonic group previous to that of the one carbon double-linking.

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[1]) *Helv. chim. acta* **2** (1919), 352. — [2]) *Berl. Berichte* **45** (1912), 3314; *Report* April **1913**, 134. — [3]) *Berl. Berichte* **49** (1916), 55, 168.

In a paper published recently, Ruzicka[1]) deals with the preparation of polymethyl-*cyclo*hexenones of the *irone type*. He succeeded in two cases, *viz.*:— Δ^2-1.1.2-trimethyl-*cyclo*hexene-6-one and Δ^2-1.1.2.5-tetramethyl*cyclo*hexene-6-one —, the yields, however, were extraordinary low and hardly permitted of the preparation of the corresponding semicarbazones. For this reason, we abstain from entering into details on this paper which, as we own, offers many interesting results in theoretical respect.

Iso*dicamphor*. — Some time ago, A. Haller[2]) demonstrated that sodiocamphor reacts readily with ketones and aldehydes with formation of bodies of the general type of diphenylcamphomethane:— $C_8H_{14}\begin{cases}C:C(C_6H_5)_2\\ \\ CO\end{cases}$. In a like manner, M. Guerbet[3]) expected to obtain bornylene camphor[4]) by interaction of camphor with sodiocamphor. This body is actually formed on heating camphor with a solution of sodium in methyl alcohol, but in very minute quantity; the chief product was a body $C_{20}H_{30}O$ which the author termed *iso*dicamphor and which is isomeric with Oddo's[5]) dicamphor (m. p. 155 to 156°) formed, *inter alia*, on action of water on the reaction-product from sodium and bromocamphor.

$$\underset{\text{Camphor.}}{C_8H_{14}\begin{cases}CH_2\\ \\ CO\end{cases}} + \underset{\text{Camphor.}}{\begin{cases}H_2C\\ \\ OC\end{cases}C_8H_{14}} = H_2 + \underset{\textit{Iso}\text{dicamphor.}}{C_8H_{14}\begin{cases}CH{-}CH\\ | \quad |\\ CO \quad CO\end{cases}C_8H_{14}}$$

For the preparation of *iso*dicamphor, Guerbet heated camphor with a solution of sodium in methyl alcohol under pressure (in a closed beer bottle) for three times 24 hours in a water-bath; the methyl alcohol and the excess of camphor is then driven off by steam-distillation and the residue, impure *iso*dicamphor, purified by recrystallisation from alcohol. 100 g. camphor yielded 25 g. dicamphor. The mother-liquors contained a second body, the nature of which Guerbet was not yet able to investigate. The bornylene camphor mentioned above results in this reaction only on raising the temperature to 180°. After crystallisation from alcohol, *iso*dicamphor forms small rhombohedra, m. p. 196°, with a weak smell recalling camphor; $[\alpha]_D + 64°\,54'$ (one-half gramme-molecule dissolved in one liter of absolute alcohol). On heating to 200° the body sublimed nearly without decomposition; at 250°, it is retransformed into camphor. The monoxime melted at 160°, the dioxime at 235°. When dissolved in carbon disulphide, *iso*dicamphor reacts with bromine with formation of monobromo *iso*-dicamphor (m. p. 161°) and dibromo *iso*dicamphor (m. p. 132°), the latter originating also on treatment, in a sealed tube, of *iso*dicamphor with the calculated amount of bromine to 100°. When oxidised with diluted nitric acid, *iso*dicamphor yields camphoric acid.

Guerbet points out finally that the same process in the formation of *iso*dicamphor — the splitting of one hydrogen atom each from two molecules of camphor in presence of an alcoholate — has been observed by Haller[6]) when heating camphor with the sodium compounds of propylalcohol, *iso*butyl, and benzyl alcohols. Here, in addition to the alkyl camphors and alkyl borneols, the corresponding alkylidene camphors were fromed from the alkyl camphors by loss of water.

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[1]) *Helv. chim. acta* **2** (1919), 144. — [2]) *Compt. rend.* **142** (1906), 971. — [3]) *Ibidem* **166** (1918), 1049. — [4]) *Ibidem* **149** (1909), 934; *Report* April **1910**, 179. — [5]) *Gazz. chim. ital.* **27** (1897), I. 159. — [6]) Compare, for instance, *Compt. rend.* **142** (1906), 1309; *Report* October **1906**, 134.

Phenols and Phenol Ethers.

Phenols insoluble in alkali. — The phenols are generally soluble in aqueous alkalies, some of them, however, being known to be insoluble. On these R. Adams[1]) reports in a paper entitled, "Alkali-insoluble Phenols". Basing on extensive theoretical considerations and on the investigation of the phenylhydrazones of various *o*-hydroxyaldehydes and -ketones the author arrives at the conclusion that the solubility in 10 per cent. aqueous alkali is lowered by introducing any atom or group of atoms into the molecule of these bodies. He explains the insolubility of certain phenols in alkalies with regard to the strong tendency of their alkali salts to hydrolysis and to the nearly complete insolubility of the phenols in water. On the other hand, several derivatives of nitrophenols are known to show, contrary to expectation, increased solubility in alkalies. This phenomenon may be explained by assuming the formation of aci-nitro compounds which are stronger acid than the phenols.

In the experimental part of his paper, Adams deals with derivatives of pæonol and of salicylic aldehyde. Of the former, the following are insoluble in alkalies:— pæonol azine (m. p. 226 to 227°), pæonol 2.4.6-tribromophenylhydrazone (m. p. 162°), bromopæonol phenylhydrazone (m. p. 172.5 to 173.5°), bromopæonol *p*-bromophenylhydrazone (m. p. 189.5°), and bromopæonol 2.4.6-tribromophenylhydrazone (m. p. 169 to 171°). Other derivatives were very difficultly soluble, some of them on heating only.

Additive compounds of phenols. — R. F. Weinland and G. Bärlocher[2]) published a communication on compounds formed from phenols, phenol ethers, or salicylic aldehyde, with neutral salts. In an earlier investigation Weinland and W. Denzel[3]) had found that pyrocatechol combines with alkali carboxylates, with potassium benzenesulphonate, or calcium chloride forming compounds which were comparable to the aquo salts, *i. e.* which are so constituted that the pyrocatechol is connected to the metallic atom by means of a secondary valency of one of the hydroxylic oxygen atoms. Weinland and Bärlocher continued the study of the additive capacity of the phenols and found that the compound of pyrocatechol-calcium chloride-ethyl alcohol mentioned above is the representative of a series existing also with other calcium halides and alcohols. Furthermore, they established the fact that in addition to quinol, pyrogallol, and phloroglucinol, the phenolic ethers guaiacol, eugenol, and vanillin combine with the potassium salts of the lower aliphatic acids thus forming similar compounds, and that equally salicylic aldehyde forms well-crystallising bodies with the same salts. Concerning the constitution of these compounds, the authors consider the compounds of the potassium salts to be either substitutive or additive compounds (*"Einlagerungs-"* or *"Anlagerungsverbindungen"*), the guaiacol compound for instance:—

$$[K(C_6H_4[OH][OCH_3])_2]O\cdot COCH_3 \quad \text{or} \quad \left[K\begin{matrix}(C_6H_4[OH][OCH_3])_2\\ O\cdot COCH_3\end{matrix}\right]$$

The compound from potassium acetate and eugenol separates from alcoholic solutions of one mol. potassium acetate and 3 to 6 mol. eugenol in shape of a finely crystalline powder which at first is coloured brown, but turns white on prolonged washing with alcohol.

From alcoholic solutions of 1 mol. $H\cdot COOK$ and 2 mols. vanillin, the compound of 1 mol potassium formiate with 2 mol. vanillin is obtained; white, matted crystals of silky lustre smelling strongly of vanillin.

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[1]) *Journ. Americ. chem. Soc.* **41** (1919), 247. — [2]) *Berl. Berichte* **52** (1919), 147. — [3]) *Ibidem* **47** (1914), 2244, 2990.

From alcoholic of 1 mol. $CH_3 \cdot COOK$ and 2 to 3 mols. vanillin there results, on gradual evaporation, the compound of potassium acetate and vanillin, small, strongly refractive crystals of rhombohedrical appearance.

The vanillin-sodium acetate compound separates from alcoholic solutions of 1 mol. $CH_3 \cdot COONa$ and 2 mols. vanillin in form of small fine needles grouped to radiated spheric crystals.

With potassium propionate, vanillin forms two compounds. One of them, $C_2H_5 \cdot COOK + 1\,C_6H_3(CHO)(OCH_3)(OH)$ crystallises from a hot concentrated alcoholic solution of 1 mol. $C_2H_5 \cdot COOK$ and 2 mols. vanillin in form of thin, white, lustrous laminæ. The other compound, $2\,C_2H_5 \cdot COOK + 3\,C_6H_3(CHO)(OCH_3)(OH)$, is obtained from alcoholic solutions (not too concentrated) of $C_2H_5 \cdot COOK$ and vanillin (1 and 4 mols. respectively) on evaporation at ordinary temperature in form of light-yellow granular crystals resembling the corresponding acetate compound. From the mother-liquor, the first-named compound crystallises out.

From solutions of 1 mol. potassium butyrate and 2 mols. vanillin, well-formed prisms of the compound of $C_3H_7 \cdot COOK$ and vanillin crystallise out on standing over sulphuric acid.

The compound of potassium acetate and salicylic aldehyde is obtained on mixing a hot, saturated of $CH_3 \cdot COOK$ in alcohol with an excess of the aldehyde; the liquid turns yellow, and on cooling, the compound separates off. In the same way, the compounds of salicylic aldehyde and potassium propionate and butyrate are obtained.

In his first treatise *on the rearrangement of phenyl allyl ethers into the isomeric allylphenols*[1]), L. Claisen gave, *inter alia*, a description of the transformation of phenol allyl ether into *o*-allylphenol. In his second publication on this interesting reaction[2]), Claisen publishes details about this rearrangement, and reports on his investigations on the reaction itself, on the *o*-allylphenyl resulting hereby, and on the phenols formed on further "allylation":— di and tri-allylphenol.

The author established that in the rearrangement reactions:—

phenol allyl ether → allylphenol
allylphenol allyl ether → triallylphenol
diallylphenol allyl ether → triallylphenol

first the one, then the other *ortho* position is occupied, and last the *para* position. Hence, *p*-allylphenol cannot he obtained by this method, and is accessible only from betel oil, as hitherto. However, Claisen hopes to realise a synthesis from 1.2.3-hydroxy-*iso*phthalic acid.

With hexahydrophenol allyl ether (*cyclo*hexanol allyl ether), no rearrangement could be effected, neither by prolonged boiling nor by superheating in a sealed tube. The reaction, therefore, seems to depend on the presence of cyclic double-linkings or centric bonds.

Phenol allyl ether. $C_6H_5 \cdot O \cdot C_3H_5$, is obtained by boiling phenol with allyl bromide, potassium carbonate, and acetone on the water-bath. B. p. 191 to 192° (760 mm.); $d_{15^\circ}^{15^\circ}$ 0.9845. It smells strongly of geranium, and not like garlic, as was stated by Perkin. If phenol allyl ether is boiled for 6 hours in a slow current of carbon dioxide, until the thermometer has reached about the b. p. of allylphenol (220°), o-*allylphenol* (o-*charicol*) (I) o-$C_3H_5 \cdot C_6H_4 \cdot OH$ is formed, a colourless oil not congealing in freezing

[1]) *Berl. Berichte* **45** (1912), 3157. *Liebig's Annalen* **410** (1913), 21; *Report* April **1913**, 144; April **1914**, 144. — [2]) *Liebig's Annalen* **418** (1919), 69.

mixtures, and with a smell recalling guaiacol; b. p. 220° (760 mm.); 99° (12 mm.); $d_{15°}^{15°}$ 1.0255. About 4 to 6 p.c. of the phenol allyl ether taken into reaction are converted into methylcumarane (II).

o-Allylphenol is furthermore obtainable from allyl-*p*-hydroxybenzoic acid by boiling with quinoline, from allylsalicylic acid by heating with dimethylaniline, from allylsalicylic methyl ester by boiling with aniline, and from allylethersalicylic acid by heating.

The phenylurethane of *o*-allylphenol melts at 106 to 106.5°.

On treatment with dimethyl sulphate and caustic soda solution, *o*-allylphenol yields o-*allylphenol methyl ether* (o-*esdragole*), *o*-$C_3H_5 \cdot C_6H_4 \cdot OCH_3$, a colourless oil of a smell like anisole; b. p. 207° (761 mm.); 86 to 87° (12 mm.); $d_{15°}^{15°}$ 0,9770. When boiled with methylalcoholic potash, *o*-esdragole is converted into *o*-anethole. The ozonide of *o*-esdragole is highly explosive; on decomposing its solution in ethyl acetate by mixing with zinc dust and glacial acetic acid, *o*-methoxyphenylacetaldehyde, *o*-$CH_3O \cdot C_6H_4 \cdot CH_2 \cdot CHO$, a pleasantly-smelling oil, is formed.

o-Allylphenol, on boiling with acetic anhydride and potassium acetate, is converted into the acetate, a colourless oil of the b. p. 238.5 to 239° (757 mm.); 117 to 118° (15 mm.).

o-*Propenylphenol* (o-*anol*) (III), o-$CH_3 \cdot CH : CH \cdot C_6H_4 \cdot OH$, results from *o*-allylphenol on dissolving the latter in three times its weight of strongest methylalcoholic potash solution; after distilling off a part of the methylalcohol the residue is boiled for an hour or two in an oil-bath. *o*-Propenylphenol boils at 230 to 231° and shows a tendency to resinify readily.

As mentioned above, *o*-allylphenol methyl ether, on prolonged boiling with strong methylalcoholic potash, is readily converted into o-*anethole*, *o*-$CH_3 \cdot CH : CH \cdot C_6H_4 \cdot OCH_3$, a colourless oil with a pleasant smell; b. p. 223 to 224° (751 mm.); 104 to 105° (13 mm.); $d_{15°}^{15°}$ 0.996[1]). On oxidation with $KMnO_4$, it passes over into salicylic acid methylether, m. p. 100 to 101°.

o-*Propylphenol*. *o*-$C_3H_7 \cdot C_6H_4 \cdot OH$, is obtained either by direct hydrogenation with palladium and hydrogen of *o*-allylphenol, or by hydrogenating allylsalicylic acid to propylsalicylic acid (m. p. 91.5°) and splitting-up of the latter by boiling with dimethylaniline. Colourless oil, b. p. 220 to 220.5° (760 mm.); $d_{15°}^{15°}$ 1.000; phenylurethane, m. p. 111°.

o,o-Diallylphenol, obtainable by allylating salicylic acid and salicylic aldehyde, is prepared more readily by rearrangement of o-*allylphenol allyl ether*, *o*-$C_3H_5 \cdot C_6H_4 \cdot OC_3H_5$, which in turn is obtained from allylphenol, allyl bromide, potassium carbonate, and acetone. Colourless oil with a smell reminding of phenol allyl ether, but weaker; b. p. 104 to 105° (10 mm.); $d_{15°}^{15°}$ 0.9675. On heating the ether in a CO_2 atmosphere, or preferably on boiling with dimethylaniline it is converted into o,o-*diallylphenol*, colourless oil with an odour reminding of cloves and thyme. B. p. 256 to 257° (770 mm.); 122° (11 mm.); $d_{15°}^{15°}$ 0.9920; phenylurethane, m. p. 141 to 142°. *o*-Diallylphenol is also formed by splitting-up of diallyl-4-hydroxybenzoic acid.

By hydrogenation, diallylphenol passes over into o,o-*dipropylphenol*, m. p. 28°; b. p. 256° (764 mm.); phenylurethane, m. p. 125°.

From 3.5-diallylsalicylic acid (IV) there results, on boiling with dimethylaniline, *o,p*-diallylphenol (V), a colourless oil of a faint clove-like smell; b. p. 266 to 268° (750 mm.); phenylurethane, m. p. 88 to 88.5°.

3.5-Dipropylsalicylic acid, m. p. 100 to 100.5°, readily accessible from diallylsalicylic acid by hydrogenation according to Paal-Skita, yields on boiling with dimethylaniline, o,p-*dipropylphenol*, a colourless oil of but weak smell; b. p. 263° (747 mm.); 130° (11 mm.); phenylurethane, m. p. 131°.

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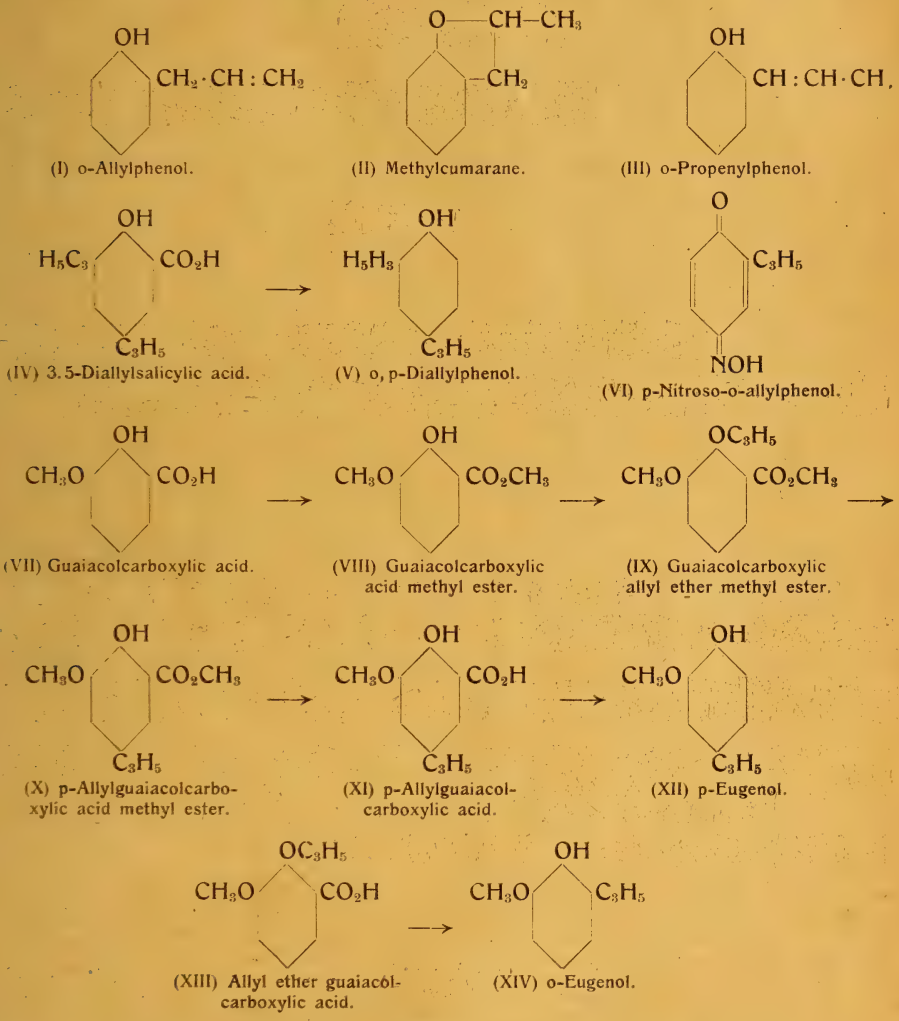
[1]) Comp. v. Auwers, *Liebig's Annalen* **413** (1917), 285, 290, 298.

The final product, on thorough allylation, of salicylic and *p*-hydroxybenzoic acids, and of salicylic and *p*-hydroxybenzoic aldehydes, is *o, o, p*-triallylphenol, since the resulting triallyated bodies, on heating, on account of the displacements of COOH and CHO taking place are split up, without exception, into carbon dioxide or monoxide, and triallylphenol. The latter is prepared easier by rearrangement of o,o-*diallylphenol allyl ether*. resulting on heating diallylphenol, in alcohol, with allyl bromide and potassium



carbonate on the water-bath; faintly-smelling liquid, b. p. 132.5 to 134° (11 mm.); $d^{15°}_{15°}$ 0.9548. When heating this ether in a current of CO_2, favourably with dimethylaniline, o, o, p-*triallylphenol* is formed, a colourless oil with a weak, persistent, rather unpleasant smell reminding somewhat of phosphines. B. p. 293 to 295° (760 mm); 158 to 159° (14 mm.); $d^{15°}_{15°}$ 0.9785. Its acidity is very low, and in order to obtain a tolerably clear solution, 80 to 100 volumes of standard potash solution are required, from which ether extracts the phenol nearly completely. Phenylurethane, m. p. 97°.

On hydrogenation, this phenol leads to o,o,p-*tripropylphenol*, an oil of faint, but not unpleasant smell; b. p. 288 to 289° (764 mm.); 156 to 157° (14 mm.); phenylurethane, m. p. 131.5 to 132°.

The cyclo*hexanol allyl ether* mentioned above is obtained on boiling a benzene solution of *cyclo*hexanol with sodium and allyl bromide; oil of a very unpleasant smell, b. p. 169 to 172° (740 mm.; $d_{15°}^{15°}$ 0.8960.

Claisen furthermore gives a description of various nitroso and amino derivatives of mono- and diallylphenols.

p-*Nitroso*-o-*allylphenol* (VI), or *alylquinone monoxime* is easily obtained, in form of its sodium salt, by treating allylphenol with the calculated quantities of amyl nitrite and concentrated sodium methoxide in methylalcohol. The free nitrosophenol melts 100 to 101°. On reduction of the sodium salt with hydrogen sulphide in ammonia, p-*amino*-o-*allylphenol* results; m. p. 113.5 to 114°. Heating with acetic anhydride converts the latter into p-*acetamino*-o-*allylphenol*, m. p. 93°.

Diallylphenol furnishes, on treatment with amyl nitrite and methylalcoholic sodium methoxide, p-*nitroso*-o,o-*diallylphenol* or *diallylquinone monoxime*, m. p. 142 to 143°, yielding on reduction p-*amino*-o,o-*diallylphenol*, m. p. 78.5°.

The rearrangement of the allyl ether has been investigated by Claisen likewise with the aminophenols; the resulting bodies, however, being but of minor interest for our special domain, we omit dealing with them.

Finally, Claisen reports on a *synthesis of eugenol*. In an earlier paper[1]) he had stated that in the transposition of guaiacol allyl ether not the ordinary (*p*-allylguaiacol) results, but an isomeride (*o*-allylguaiacol, *o*-eugenol). When, however, the *ortho* position in guaiacol is blocked and then the allyl ether prepared, one arrives, after performing the transposition, at a derivative of *p*-eugenol, from which the latter itself is obtainable simply by removing the blocking group. One starts best from guaiacolcarboxylic acid (VII), from which first the methyl ester (VIII), then the allyl ether methyl ester (IX) is prepared. On subjecting the latter to the rearrangement, the methyl ester of *p*-allylguaiacolcarboxylic acid (X) results. The free acid (XI) is split up, by boiling with dimethylaniline, into CO_2 and *p*-eugenol (XII). *o*-Eugenol is obtained from the methyl ester (IX) *via* the allyl ether of guaiacolcarboxylic acid (XIII) which on heating yields *o*-eugenol (XIV).

Methyl guaiacol carboxylate (VII) is obtained best by boiling the acid with methylalcohol and sulphuric acid; m. p. 66 to 66.5°. On boiling this ester, in methyl ethyl ketone solution, with allyl bromide, potassium carbonate, and potassium iodide, the ether-ester (IX) (2-allyloxy-3-methoxybenzoic acid methyl ester) is formed; b. p. 165 to 167° (8 mm.). The free acid melts at 65°. When heated in an oil-bath, it passes over into *o*-eugenol (b. p. 250 to 251° at 760 mm.).

The ether-ester (IX), when heated to 230 to 240°, in order to effect the transposition, is apt suddenly to begin to boil very violently, with simultaneous rise of the temperature up to 300°; hence it is recommended to start the isomerisation by heating under reduced pressure, which takes place at 200° under 60 mm. The resulting ester (X) (2-hydroxy-3-methoxy-5-allylbenzoic ester) melts at 55 to 55.5°; the free acid (XI) at 127°.

When heated with dimethylaniline, the acid splits off CO_2 at 160°, and after three-quarter hour's boiling the rearrangement is perfected. The *p*-eugenol obtained boiled at 254° (760 mm.); phenylurethane, m. p. 95.5°; *p*-nitrobenzoate, m. p. 81°.

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[1]) *Berl. Berichte* **45** (1912), 3161. *Liebig's Annalen* **401** (1913), 50. *Report* April **1913**, 144.

Eugenol is also obtainable, in a satisfactory yield, on boiling the methyl ester of C-allylguaiacolcarboxylic acid (X) with aniline.

On the *phenylurethanes of various phenols*, see pp. 20 and 130 of the present *Report*.

As to the preparation of *carvacrol from spruce oil*, comp. pages 57 *et seq.* of this *Report*.

Acids.

Spatial rearrangement of the chlorides of dibasic alicyclic acids. — Apart from the usual processes employed for rearranging the geometrical isomerides of dibasic acids of the alicyclic series, the carboxyl groups of which are contained in different side-chains, Marsh[1]) had found that *d*-camphoric acid chloride, on treatment with water, yields not only the original *d*-camphoric acid, but in addition the geometrical isomeride, l-*iso*camphoric acid. This method has been applied by O. Aschan and A. Havulinna[2]) to various acids. They examined whether the sterical rearrangement occurs already in the formation of the acid chlorides, or in heating or distilling the chlorides, or on decomposing them with water, and undertook these experiments with each one representative of the camphoric, *iso*fenchoric, and camphenic acid series. The result of their investigation was that a great difference was found to exist in the behaviour, on hydrolysis, of the distilled and the non-distilled chlorides, the rearrangement evidently taking place already during the formation or the storing of the chlorides and not only during the action of water. l-*Iso*camphoric acid (from *d*-camphoric acid with hydrochloric and glacial acetic acids at 180 to 185°) yielded, after conversion into the chloride and decomposition of the latter with water, a mixture of l-*iso*camphoric and *d*-camphoric acids; the latter was again transformed, in the same manner, into l-*iso*camphoric acid. *cis*-Camphenic acid, after conversion into the chloride and decomposition of the latter with water, is transformed only in minute quantities into *trans*-camphenic acid. On distillation, however, *cis*-camphenic chloride is partly converted into the *trans*-isomeride, the latter undergoing the same rearrangement on distillation, with partial formation of *cis*-camphenic chloride. The same holds good for *cis*-d,l-*iso*fenchocamphoric acid, whose chloride, on decomposition, is partly converted into the *trans*-isomeride, and *vice-versâ*.

Cinnamic acids. — In addition to the storax cinnamic acids, according to E. Erlenmeyer jun.[3]), two other normal cinnamic acids exist, the so-called heterocinnamic acids which may be isolated from synthetic cinnamic acid. Riiber and Goldschmidt[4]), however, pointed out that the differences between synthetic and storax cinnamic acid observed by Erlenmeyer might be ascribed to the presence of impurities in the synthetic product, and actually succeeded in isolating a chlorinated cinnamic acid from commercial synthetic acid. Although Erlenmeyer[5]) disproved the objection, A. W. K. de Jong[6]), on studying Erlenmeyer's work, was still under the impression that his heterocinnamic acid is an impure acid and that to this impurity is due the difference found by him between that acid and common cinnamic acid. For this reason, de Jong prepared absolutely pure cinnamic acid and investigated whether this acid, prepared

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[1]) *Chem. News* **60** (1889), 307. — [2]) *Öfversigt af Finska Vetenskaps-Societetens Förhandlingar* **59** (27. 1. 1917); *Chem. Zentralbl.* **1918**, II. 953. — [3]) *Berl. Berichte* **42** (1909), 502; *Report* April **1909**, 138. — [4]) *Ibidem* **43** (1910), 453; *Report* April **1910**, 189. — [5]) *Ibidem* **43** (1910), 595; *Report* October **1910**, 203. — [6]) *Kon. Akad. Wetensch.* Amsterdam, *Wis- en Natuurk. Afd.* **27** (1919), 894. (Meeting of Dec. 28, 1918.)

according to Erlenmeyer's directions, was able to yield synthetic cinnamic acid with the properties indicated by Erlenmeyer.

With this aim, de Jong saponified the oil from the rhizomes of *Alpinia malaccensis* known to consist, for the major part, of methyl cinnamate. The saponified oil was repeatedly shaken out with benzine, the acid thrown down and after washing out oxidised with potassium permanganate. Owing to the presence of impurities, the mass frothed considerably, and the cinnamic acid was therefore dissolved in sodium carbonate solution, the latter shaken out with benzine and then acidulated. Thus purified, the acid did froth no more on oxidation with permanganate. Cinnamic acid prepared according to Perkin separated off, in Erlenmeyer's ether test, well-formed crystals of α-cinnamic acid which showed no appreciable difference from the original acid.

The cinnamic acid was then treated, following Erlenmeyer's directions, with caustic soda solution, but leaving one-sixth of the acid present in the free state. By this means, the author expected to obtain Erlenmeyer's heterocinnamic acid, which, however, was not the case. The crystals, it is true, differed somewhat from the original crystals in their appearance. Since this discrepancy from the common acid might be explained by a contamination, further purification was resorted to.

de Jong purified the methyl cinnamate from alpinia oil several times until the m.p. 34° was reached. The ester was oxidised to benzaldehyde and the latter converted into cinnamic acid. Tested by the "ether test", it yielded crystals of α-cinnamic acid, but revealed not the properties claimed by Erlenmeyer for synthetic cinnamic acid. Neither did the "caustic soda test" lead to heterocinnamic acid.

By further purifying the ester by means of recrystallising under special precautions, the m. p. was finally raised to 34.8 to 34.9°. From this ester, 16.5 g. synthetic cinnamic were prepared according to Erlenmeyer's directions; the first fraction (about 1 g.) yielded, in the "ether test", Erlenmeyer's so-called synthetic cinnamic acid.

It was not possible to obtain Erlenmeyer's synthetic acid by recrystallising the cinnamic acid (from alpinia oil) purified by water.

From 860 g. cinnamic acid, the author obtained, on purification by aid of alcohol, 13.5 g. of a synthetic acid, of which the first fraction (about 1 g.) represented Erlenmeyer's synthetic acid.

de Jong concludes from the results of his investigations that Erlenmeyer's heterocinnamic acid is not formed from pure cinnamic acid in the manner described by him. Its formation must be attributed to the presence of impurities in the cinnamic acid used by that author. The heterocinnamic acids of Erlenmeyer, therefore, are no uniform chemical products.

Owing to the investigations of S. V. Hintikka[1]), P. Lipp[2]), and of Komppa and Hintikka[3]), *camphenic acid* (camphene camphoric acid) (III) has been recognised as a 1.3-carboxy*cyclo*pentyl*iso*butyric acid. Since these papers have appeared, but little more has been published on that subject. However, a publication by Hintikka[4]) has only now become generally known. The author reports on the conversion of carbocamphenilonone (II) into hydroxycamphenilanic acid (I) by heating with dilute caustic soda on a water-bath, by which reaction the formula for carbocamphenilonone was verified. According to Aschan[5]), camphenic acid, on distillation under ordinary

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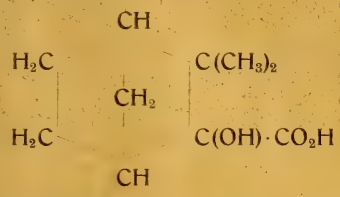
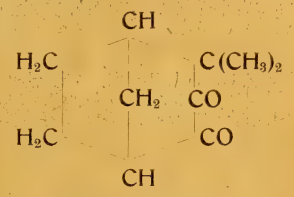
[1]) *Berl. Berichte* **47** (1914), 512; *Report* April **1914**, 145. *Ann. Acad. Scient. Fenn.*, A. **5** (1914), No. 3; *Report* April **1915**, 107. — [2]) *Berl. Berichte* **47** (1914), 871; *Report* April **1915**, 105. — [3]) *Berl. Berichte* **47** (1914), 1550; *Report* April **1915**, 106. — [4]) *Ann. Acad. Scient. Fenn.*, A. **6** (1914), No. 3; *Chem. Zentralbl.* **1919** I. 839. — [5]) *Liebig's Annalen* **383** (1911), 58.

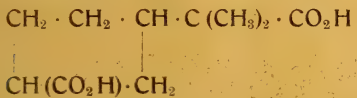
pressure, passes over into a liquid unsaturated acid $C_9H_{14}O_2$ and a solid acid $C_{10}H_{14}O_3$, m. p. 134°. The former is, in all probability, constituted according to formula (IV), since it yields, on reduction with hydrogen in presence of palladium, an acid $C_9H_{16}O_2$ which seemed to be identical with Bouveault and Blanc's[1]) dihydrocamphoceënic acid (V). The acid is stable towards potassium permanganate; b. p. 138 to 139° (10 mm.); amide, m. p. 169°. For sake of comparison with this acid $C_9H_{16}O_2$, the author prepared, from *cyclo*pentanone, *cyclo*pentane *iso*butyric acid (VI), by reducing Wallach's[2]) ethyl *cyclo*pentene *iso*butyrate in alcoholic solution with hydrogen and colloidal palladium



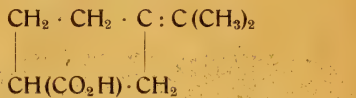
(I) Hydroxycamphenilanic acid (camphenylic acid).



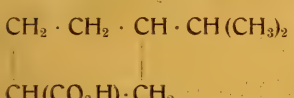
(II) Carbocamphenilonone.



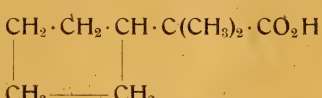
(III) Camphene camphoric acid.



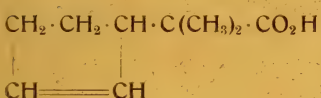
(IV) ? Acid $C_9H_{14}O_2$ from camphene camphoric acid



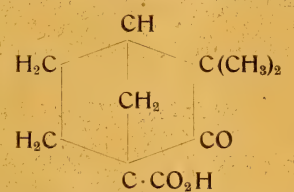
(V) Dihydrocamphoceënic acid.



(VI) *Cyclo*pentane *iso*butyric acid.



(VII) *Cyclo*pentene *iso*butyric acid.



(VIII) Camphenilone-α-carboxylic acid.

and saponifying the resulting saturated ester with sodium ethoxide. Amide of the saturated acid, m. p. 141 to 142°; amide of *cyclo*pentene *iso*butyric acid, m. p. 136 to 137°. The formation of *cyclo*pentene *iso*butyric acid (VII) in the degradation of camphenic acid is quite possible.

The acid $C_{10}H_{14}O_3$ was proved to be a ketonic acid, in harmony with Aschan's assumption; it yields a phenylhydrazone (m. p. 142 to 143°) and passes over, on careful heating with caustic potash or on boiling with sodium methoxide or ethoxide, into *cis-d,l*-camphenic acid. It must be regarded, therefore, as camphenilone carboxylic acid (VIII) and is, in all probability, identical with Houben and Willfroth's[3]) camphenilone carboxylic acid.

Hintikka investigated, furthermore, the behaviour of several salts of camphenic acid on dry distillation. Whilst the lead salt yields camphenilone, as was demonstrated

---

[1]) *Compt. rend.* **146** (1908), 233; **147** (1908), 1314; *Report* April **1908**, 191. — [2]) *Liebig's Annalen* **353** (1907), 305; *Report* October **1907**, 177. — [3]) *Berl. Berichte* **46** (1913), 2283; *Report* October **1913**, 150.

previously, other salts, *e. g.*, the calcium salt, yield no such ketone. The ferric salt, obtained from the ammonium salt by precipitation with ferric chloride, yields on dry distillation but a small amount of camphenilone, the uranyl salt (from the ammonium salt with uranyl acetate) gives a somewhat better yield, whilst the copper salt yields not a trace.

Nitrogenous Bodies.

Hydrocyanic acid. — It may be taken for universally known that numerous plants develop hydrocyanic acid when put in contact, or distilled, with water[1]). Those of our readers who take interest in this question are referred to a paper published recently by L. Rosenthaler[2]), where the theories put forward by the various investigators on the physiological rôle of that acid are dealt with critically and where a synopsis is given on the plants hitherto known to produce hydrocyanic acid. The corresponding bibliography is given in full.

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed. vol. I, p. 531. — [2]) *Schweiz. Apotheker Ztg.* 57 (1919), 267, 279, 321.

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ANNUAL REPORT

on

Essential Oils, Synthetic Perfumes, &c.

Published by

SCHIMMEL & Co.

MILTITZ

near Leipzig

APRIL/OCTOBER 1920.

Sole Agents in the United States and Canada
FRITZSCHE BROTHERS, INC.
82-84 BEEKMAN STREET, NEW YORK CITY.

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Distillation of Cananga flowers in Java.

(After a water-colour painting in the possession of the Perfumery Department of the German Museum in Munich. Gift of the firm of Schimmel & Co.)

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List of abbreviations.

d = specific gravity.
$d_{20°}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d^{20°}_{4°}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
$n_{D20°}$ = index of refraction at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid. v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.
The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Commercial Notes and Scientific Information on Essential Oils.

Ajowan Oil. — The attempts to cultivate the Ajowan plant *Carum copticum*, Benth., in Montserrat were further continued. The yield per acre in 1918 was 360 to 471 lbs. of seed, against 1128 lbs. per acre in the year preceding[1]). In view of the high costs in gathering the individual seeds, an attemps was made to distil the oil from the complete plant containing the ripening fruit. Out of 100 lbs., 14.2 ozs., *i. e.* 0.9 per cent. of an oil was obtained with the following characteristics: — $d_{16,5°}^{30°}$ 0.8740; $\alpha + 0.58'22''$; $n_{D30°}$ 1.4806; phenol content 23.3 per cent. (?)[2]), thymol content 1.57 per cent.[3]) Further the ripe uncrushed seeds were subjected to distillation yielding 2.5 per cent. of an oil, having a thymol content of 36 per cent. Before, from the crushed seeds 2.7 and 3.1 per cent. of oil was obtained with 43 and 54 per cent. thymol content respectively[4]).

In trade two kinds of ajowan seed are recognized, "Indore" and "Kurnool", the latter being the better. The following table, which gives a survey of the quantities of ajowan seed exported from India since 1912, has been taken from the recently published *Handbook of Commercial Information for India*, Calcutta 1919.

	Amount	Value
1912/13	21650 cwt.	£ 6135
1913/14	9784 „	„ 2983
1914/15	7368 „	„ 2736
1915/16	13062 „	„ 4871
1916/17	11093 „	„ 4304
1917/18	3990 „	„ 2765
1918/19	1917 „	„ 2102.

Of the export which is not very important, 97 per cent. goes via Bombay, the remainder via Calcutta; and only a very small quantity via Madras. Formerly 80 per cent. of the exported seed was used by Germany; at present, when the export is greatly diminished, about 25 per cent. goes to Great Britain.

In its native country the seeds are used in great quantities for the preparation of spices (curry), *Pan supari*[5]) and *Omam water*. This liquid, obtained by distillation of seeds, is sold as an essential oil in all the larger cities of India, and together with thymol (*Ajwan-Ka-phal* = flowers of ajowan) is used as a medicine, especially for cholera.

Apparently two firms in India have at last succeeded in obtaining thymol crystals from ajowan oil, which were formerly prepared in Germany only. 10500 lbs. of these

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[1]) Cf. *Report* **1919**, 5, 75. — [2]) This appears to be a printer's error. — [3]) We obtained an oil from fresh plants cultivated in Miltitz, containing about 1 per cent. thymol, and small quantities of phellandrene (*Report* October **1903**, 78). — [4]) *Perfum. Record* **10** (1919), 214. — [5]) *Pan Sooporee*, prepared chiefly from betel leaves and areca nuts, used for chewing, and also for ceremonial purposes in leave-taking.

during the last two years, till the end of June 1919 worth £ 160000 were exported to America and Great Britain. With regard to this we must say, that according to our experience, the thymol of English origin leaves much to be desired. The article which we recently received from London, was of a yellow to brown colour and smelled like inferior oil of thyme.

Almond Oil, bitter. — We entirely repeat what was already said in the last reports, when we call attention to the fact, that yet again great abuse is made of the designation "Bitter almond oil, genuine, free from hydrocyanic acid". All oils sent to us for our opinion thereon, contained chlorine without exception, and consisted at least partly of ordinary chlorine-containing benzaldehyde. Only in one solitary case was an adulteration of another kind established, about which we will here say a few words. The oil in question behaved as follows:— $d_{15°}$ 1.123, acid value 20.5 = 4.5 per cent., reckoned as benzoic acid, soluble in 1.7 volumes and more of 50 per cent. alcohol. Hydrocyanic acid and chlorinated compounds were not present. First the high specific gravity of the oil was remarkable (normal 1.050 to 1.055°), which could not in this case be explained by the presence of a great proportion of benzoic acid, which could have been formed on standing by oxidation of the benzaldehyde. Besides, the very ready solubility was suspicious, for otherwise about 8 volumes of 50 per cent. alcohol are necessary for the solution of bitter almond oil. The further examination very soon gave information as to the cause of the discrepancies. It turned out that the oil had been adulterated with glycerin ester, which was recognised as such by its components (glycerin and acetic acid). From the high specific gravity and the ester value (418; a pure benzaldehyde, saponified for comparison, gave a value of 18.7), it is to be assumed that the added quantity of glycerin ester amounted to about 50 per cent.

As long as apricot kernels of Chinese, Californian and Syrian origin, which already are again appearing on the European markets in fair quantities, are still offered at prices of about M. 15 per kilo, will one do without the earlier preparation of genuine bitter almond oil which was carried out in grand style, and in future must make use of the artificial, chlorine-free benzaldehyde as a worthy substitute, which indeed stands at his disposal and at a modest price. (See p. 64 of this *Report*.)

Oil of Amomis jamaicensis. — On the calcareous soil of "Upper Clarendon" (Jamaica) and on the "Dry Harbour" Mountains (Jamaica) at an altitude of from 2000 to 2500 ft., the wild pimento flourishes, a new kind, *Amomis jamaicensis*, Britton and Hill, which grows to a height of 40 ft., with a trunk a foot thick. A bright-yellow pleasant smelling oil can be distilled from the leaves of this Myrtacea, which oil smells like that of *Lavandula Spica*, DC. 100 lbs. of leaves yielded 202 cc. oil with the following characteristics: — $d^{15°}_{15°}$ 0.8895, $\alpha_{D20°}$ — 6°, A.V. 2.4, E.V. 4.2 (corresponding to 1.5 per cent. ester, reckoned as $C_{10}H_{17}OCOCH_3$), E.V. after acetylating 129.4 (corresponding to 39.4 per cent. of total alcohol, reckoned as $C_{10}H_{17}OH$). The oil was soluble in 2.5 volumes of 70 per cent. alcohol at 15° C. and became cloudy with 6 volumes. During the distillation no components heavier than water separated out, as is the case with oil of bay. The oil contained chiefly *l*-linalool, but hardly any phenols, and hence is distinguished from the ordinary pimento and pimento leaf oil, which are both rich in eugenol. Although the wild pimento is pretty widely distributed, the obtaining of the oil in large quantities under present conditions would hardly be a commercial success[1]).

[1]) *Bull. Imp. Inst.* 17 (1919), 297.

Angelica Oil. — The prospects of obtaining sufficient quantities of the root suitable for distillation are also this year very unpromising. Both Thuringia and the Saxon angelica territory have at their disposal only a moderate crop, but the prices demanded are absolutely prohibitive; and hence the price of angelica oil will be such, that many users of it will have to do without. Only the fact that we have foreign orders on hand for the oil, which must be reckoned with, has caused us to buy some. Unfortunately our own growths will yield crops only next year.

Oil of Backhousia citriodora. — It was reported several years ago that the Myrtacea *Backhousia citriodora*, F. von Müller, which grows only between Brisbane and Gympy, yielding an oil containing 95 per cent. citral was being gradually extirpated[1]). Meanwhile these plants have been successfully grown in the Botanical Garden of Sydney, and proved that they can be cultivated. *Backhousia citriodora* is grown from cuttings or seed. In the second year the leaves can be cut off and subjected to distillation. 1 lb. of fresh leaves yielded 60 minims, *i. e.*, about 0.8 per cent. of oil[2]).

Bay Oil. — The difficulties of procuring the pure West Indian distillate have unfortunately not yet been removed, and consequently the great scarcity of this oil in the European markets must still be reckoned with. The demand for Bayrum has greatly fallen off on account of the prohibitive prices; especially so, as there are other hair-washes which have a pleasant and refreshing effect on the scalp.

Although cotton has become the chief article of commerce of Montserrat, yet according to a report of the Agricultural Department, the oil of bay industry is developing satisfactorily[3]). The following example shows how profitable the culture of the bay tree, *Pimenta acris*, Wight, becomes with the times. In 1908 about 800 seedlings raised in pots, were transplanted on an area of 1 acre. After $2^1/_2$ years the leaves could be cut for the first time (1368 lbs.), and 14 lbs. of oil worth £ 7 were distilled. The yield increased yearly, so that in 1917, 6516 lbs. of leaves with 71 lbs. of oil worth £ 46 were obtained. Formerly, only the leaves were cut off, but now the larger boughs six feet from the ground are sawn off and then stripped of their leaves. It is recommended to plant in the vicinity of mountains on account of the greater moisture. The phenol content of the oil, which in 1914 to 1916, on an average amounted to only 50.9 per cent., rose in 1917 again to 55.0 per cent. — the duration of the distillation being the same in both cases[4]).

Birch-bud Oil. — All efforts to procure birch-buds for distillation have remained unsuccessful, since Russia only was in the position to deliver sufficient quantities, and unfortunately contact with this country will be for some considerable time impossible. The preparers of trustworthy birch hair-waters must bow to the fact that birch-buds and birch-bud oil can hardly ever again be delivered to them in sufficient quantity, for in view of the awful conditions in Russia, it seems to us more than doubtful that anyone will take an interest in the collection of the buds.

Several large quantities of birch-sap, which now and again were offered, and of which our opinion was asked, turned out to be artificial products, which indeed were cheap, but which were scarcely distinguishable from ordinary rainwater.

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[1]) *Report* April 1913, 29. — [2]) *Perfum. Record* 10 (1919), 209. — [3]) *Ibidem* 213. — [4]) Cf. *Report* 1916, 5; *Report* 1918, 9.

Oil of Boswellia serrata. — In our *Report* of last year we inserted on page 5 a note on oil of turpentine, resin and gum of *Boswellia serrata*, which was taken from the periodical *"Die Seife"*. We now find that the original essay thereon is to be found in the *Bull. Imp. Inst.* **17** (1919), 159.

Oil of Brassica campestris, L. — According to a communication from A. Viehöver[1]) from the Pharmacognosy Laboratory, Washington, the seed of *Brassica campestris*, L., var. *chinensis, oleifera* (Chinese colza), contains from 40 to 50 per cent. of an oil similar to rapeseed- and colza oil. On macerating the seeds with water, a glucoside and the nascence of a volatile oil, present in quantity from 0.4 to 0.6 per cent., was observed. This oil was identical with the crotonyl mustard oil, earlier discovered in rapeseed, *Brassica Napus*, L., with which the formula $SCN \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$ agrees[2]).

Camphor Oil. — Several thousand cases of raw camphor oil have lately arrived at our establishment, and the manufacture of this most important raw commodity has again been partially taken up.

The export of camphor oil from Japan in the first six months of the year was as follows: —

	1918	1919	1920
Kin	539 623	266 439	1 221 649
Yen	108 069	66 244	537 267

How considerably this export has recovered is seen from the fact that in the month of June 1920 alone 152 288 Kin to the value of 37 060 Yen were shipped, that is, in one month, more than a fourth of the total yearly quantity for 1919.

We cull a noteworthy compilation from a report from Osaka[3]) of the course of the camphor production in Japan and Formosa during recent years. The preparation of refined camphor in Japan is confined principally to Kobe and Osaka; for this purpose 4 million Kin of raw camphor on an average were used in the years 1915, 1916 and 1917. In the latter half of 1917 and in 1918 the camphor industry diminished greatly in consequence of the War and the scarcity of labour. As a result of the set-back in the camphor production, a great camphor concern was formed from the companies which deliver the raw camphor to the Japanese Monopoly Office. The camphor will be more systematically collected and economically managed. By this means it is thought that one will be better able to compete in the market with other industries. Whilst a grand total of at least 4 million Kin (5 291 080 lbs.) is again expected for 1919, it is hoped that for the year commencing 1st April 1920 a total of from 5 to 6 million Kin will be reached.

The following figures give information *re* the total export of refined camphor from the two chief places: —

	1915 Amount Kin	1915 value Yen	1916 Amount Kin	1916 value Yen	1917 Amount Kin	1917 value Yen
Kobe	3 899 062	3 446 400	4 121 604	4 298 684	2 452 363	4 381 271
Osaka . . .	473 972	425 072	513 416	507 959	257 003	418 822

[1]) *Perfum. Record* **10** (1919), 259. — [2]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 527. — [3]) *Drug and Chemical Markets* **7** (1920), 165.

The following quantities of raw camphor and camphor oil were produced in Japan and Formosa 1912 to 1918:—

	Crude camphor Kin	Camphor oil Kin		Crude camphor Kin	Camphor oil Kin
1912 . . .	3995400	4532600	1916 . . .	5208800	6808500
1913 . . .	4745800	4321700	1917 . . .	3233200	5045600
1914 . . .	5124800	5448800	1918 . . .	2432800	4218500
1915 . . .	4932700	5933400			

Of this, about 70 per cent. comes from Formosa, and 30 per cent. out of Japan proper. The province of Kiushiu furnishes by far the greatest part (80 per cent.) of the camphor productions. Altogether in Old Japan alone were the following quantities of raw camphor and camphor oil wore 1912 to 1917:—

	Crude camphor Kin	Camphor oil Kin		Crude camphor Kin	Camphor oil Kin
1912 . . .	976938	1687015	1915 . . .	2564869	3001426
1913 . . .	995896	1691000	1916 . . .	1564869	3001426
1914 . . .	1115500	1977294	1917 . . .	982608	1852998

The amounts of refined camphor (from raw camphor from Old Japan and Formosa) prepared in Japan are given in the following table:—

	Refined camphor Kin	Yen		Refined camphor Kin	Yen
1912 . . .	2086000	2024000	1915 . . .	4372000	3871000
1913 . . .	2319000	2028000	1916 . . .	4635000	4806000
1914 . . .	3114000	2867000	1917 . . .	2709000	4800000

These figures already show how camphor has at first gradually, and since 1917 quite considerably, increased in value. In this respect also, the following statistics re the total exports of camphor and camphor oil from Japan during the last six years are noteworthy.

	Camphor Kin	Yen	Camphor oil Kin	Yen
1914 . . .	3073800	2780000	1366900	216600
1915 . . .	3880000	3475000	2313300	318700
1916 . . .	5753800	6287700	1971600	308200
1917 . . .	3119900	5304100	1713600	316100
1918 . . .	1764200	3686300	1370800	268000
1919 . . .	2031200	7883800	1030600	333700
1920 (to February)			624100	237400

Since 1916, in which year, with 5753800 Kin to the value of 6287700 Yen, the highest level was reached, the export diminished considerably; but on the contrary the price was increased threefold. During the latter months (reckoned from 28 July 1920 onwards), however, the value of refined camphor sank continually and amounts at present to only a third of its earlier level.

Although there were hopes a short time ago, at a price of from 1.80 to 2 Yen per lb., with an output for the year of 6 million lbs., to reach a grand total of 1.3 million Yen, yet, according to the prices of today, — about 1 Yen per lb. —, this total will be reached no more.

In the year 1919 the camphor export from Japan was distributed amongst the following countries as follows:—

	Kin	Yen
British India	67 521	381 268
Great Britain	175 317	836 094
France	146 222	640 046
United States of N. America	1 569 506	5 771 899
Australia	2026	4739

From the report of the American Trade Attaché in Tokio[1]) of August 1919 we take the following statistics, which show the increasing significance of America as compared with Europe:—

	Camphor-Production in Japan.	Exports from Japan to United States of America.	Exports from Japan to Europe.
1915/16 . . .	10 389 521 lbs.	4 211 766 lbs.	1 706 277 lbs.
1916/17 . . .	11 506 447 „	6 525 489 „	1 726 997 „
1917/18 . . .	7 945 890 „	4 129 027 „	1 045 345 „
1918/19 . . .	6 137 732 „	2 055 188 „	913 021 „

Since the Monopoly Office delivered the so-called "BB" or refined camphor to Europe, and "B" or raw camphor to the United States, all the figures in the above table are given for "B" camphor. In the preparation of "BB" from "B" camphor about from 12 to 13 per cent. is lost.

In an article on Formosa, the native land of camphor, A. B. Kirjassoff[2]) gives, partly from his own personal observations, a series of interesting details about the winning of camphor in this island. Next to the cultivation of rice and sugar-cane, which is carried on on a grand scale, and promoted by the government, the population is employed in the camphor industry to a great extent. 25 years ago when the Japanese went to Formosa, this industry was a mere state monopoly. Formerly the spoliation of the camphor forests was the fashion, but the Japanese soon began to proceed more systematically, and carry on afforestation scientifically. At the present time the camphor in Formosa is still obtained from wild-growing trees, which will probably be extinct in ten years time. The "Camphor Monopoly Bureau" already 20 years ago commenced cultivating the *Cinnamomum Camphora* as a substitute. Over 10 years ago 3000 acres, and since 1919, 12000 acres, were yearly planted with camphor trees. It has been reckoned that 5 million Kin camphor can be annually obtained for the next 10 to 15 years from the wild-growing camphor trees of Formosa. Yet it is stated that the camphor forests on the island will be exhausted in 10 years. During recent months the demand in Formosa was very great; in the period from January to March (inclusive) 1920. Japan delivered 379635 lbs. to the United States of America.

It appears at first extraordinary, but it is a fact, that the savage and terrible head-hunters of Formosa were of use to the camphor industry. If these savages had not signified a continual danger to the camphor workers, the wild-growing camphor trees of Formosa would have disappeared long ago. The tree feller works constantly in the company of armed men, but in spite of this he is never sure of his life. The tales of these woodmen remind one of Indian stories, in which tomahawks, poisoned arrows, and scalping knives play an important part.

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[1]) *Bureau of Foreign and Domestic Commerce. Nachr. f. Hand., Ind. u. Landw.* 78 (1919), 7. *Handelsberichten* (Den Haag) 13 (1919), 644. — [2]) *National Geographical Magazine*, March 1920. As per *Americ. Journ. Pharm.* 92 (1920), 237.

The camphor trees mature best on moderate slopes up to a height of 4000 feet, and nowhere else in the world do they attain to such a size and girth as in Formosa. Formerly trees with a circumference of from 30 to 40 ft. were no unusual sight, but at present such samples only exist in the districts inhabited by the savages. Also a tree of medium circumference (12 ft.) yields considerable quantities, about 6660 lbs. of camphor, which are worth nearly 5000 dollars. The tree offers a fine sight with its symmetrical trunk, its long-armed branches, and its charming delicate green leaves.

Now and again one sees in the interior of the country a distilling boiler, as used by the natives, as well as by the Chinese workmen for obtaining raw camphor. Close by is generally found a blockhouse which serves as dwelling for the workman and his family. Here the raw product is packed in tin canisters, in order to be sent on to the refinery at Taihoku[1]).

According to information from various sources, the camphor production and camphor trade is again reviving in China. In our previous year's *Report* (p. 13) we pointed out, that in consequence of the thoughtless exploitation of the forests since 1907 the camphor production had still further sunk in China. The obtaining of camphor there, thanks to its furtherance by the military governor of Kiangsi, is making great advances. In one district 100000 camphor trees have been planted; a company with a capital of 400000 dollars intends to erect a factory for the winning of camphor. Already in the year 1918, 2492 piculs of camphor, 1863 piculs of camphor oil, and 1055 piculs were exported from the chief harbour of the province of Kiangsi, Kin-Kiang on the Yangtse-kiang[2]).

In the provinces also of Kwangtung and Fokien they have again devoted themselves more to the production of camphor, on account of the great demand from America; a further development of this industry is to be expected. In Kwangsi, where the camphor production up till now has been insignificant, a company has been formed in the name of the Government (according to reports from the American Consul-General in Hong Kong)[3]), which has erected a camphor factory on modern lines and intends to make this industry a financial success. In the island of Hainan the camphor cultivation is still in the experimental stage.

In 1919 the export of camphor from Hong Kong to the United States of America amounted to nearly 2 million dollars, over 100000 lbs. monthly were delivered, and in November 1919 even 164575 lbs. valued at 309719 dollars. When one bears in mind the total export of camphor to the United States — in 1919 4453060 lbs. valued at 5582331 dollars — the part which China again takes in the delivery of camphor, is recognised. Under these conditions, the prices a short time ago again fell, which the Japanese monopoly during the last three years had more than doubled.

In completion of the above the *Journal of the Society of Chemical Industry*[4]) reports:— The increasing demand for South Chinese camphor gave rise to increased activity. The Government officials of the province of Kwangsi founded a company in Kuelin, which erected an up-to-date factory for the working of camphor. The manufacture and export of camphor was newly organised everywhere. Additionally, American traders took up the camphor oil trade successfully. For example, great quantities of oil were exported from the neighbourhood of Kwangtung, Fukien and Kiangsi. The Kiangsi Province, however is regarded as the most productive territory in China; here only a small number of trees

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[1]) Further detailed accounts *re* the camphor production in Formosa are to be found in Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 447. — [2]) *Ind. u. Handelsztg.* **1920**, No. 80. — [3]) *Commerce Reports* Feb. 11th **1920**. According to *Americ. Journ. Pharm.* **92** (1920), 278. — [4]) *Ind. u. Handelsztg.* **1920**, No.141.

are felled. In the Isle of Hainan the camphor culture is still in the experimental stage. The export of camphor from the Foochow district sank in 1906 from 1516600 lbs. to 49533 lbs., since the aimless Government control, and the competition of the Formosan camphor, but more especially the former exploitation of the forests, hindered the development verymuch. In consequence of the high prices, the production again recovered somewhat in 1918, so that an export of 56533 lbs. was reached. The camphor industry, which is carried on there in completely primitive processes, still suffers from difficulties of transport. Labour, on the contrary, is cheap. The Government shows itself favourable to the restoration of the camphor industry and is said to be prepared to take upon itself at least a part of the expenses of restoration.

Total Imports of Camphor to the United States of North America[1]):—

	Quantity	Value
1917	8391850 lbs.	$ 3392132
1918	4188051 „	„ 2157062
1919	4453969 „	„ 5582331

According to another memorandum[2]) the total export of camphor from Hong Kong had

1915 of value of	$ 60087
1917 „ „ „	„ 1641205
1918 to June 30th	289710 Mexican Dollars

Of the last figure 181551 Mexican Dollars fall upon the United States.

Also camphor oil containing 60 per cent. pure camphor was forwarded to America in considerable quantities from Kwangtung, Fokien and Kiangsi. Whilst British India and the Straits Settlements took nine-tenths of the camphor export up to the beginning of 1918, the Americans have now become the greatest buyers.

P. Carmody[3]) also gives some data *re* the state of the whole camphor production. The yearly demand for camphor for the whole world is estimated at 10000000 lbs. In addition to Formosa, the Chinese province of Fokien, the two Japanese islands of Shikoku and Kiushiu, Cochin-China, Sumatra, Java and Borneo must be taken note of as regards camphor production.

In the British Colonies camphor is successfully cultivated in Ceylon, the Federated Malay States, Trinidad and Dominica. In Ceylon, where 1893, 1000 trees were raised from seed, the annual yield from the young trees is estimated at 56000 lbs. per acre. That produced in Mauritius is unsaleable.

Accordingly the successful cultivation of camphor is possible in the British Empire. The decrease of the Japanese camphor forests, as also the high price at present paid for camphor, favour a further extension of these plantings. Whilst formerly the price for camphor amounted to a little over 2 s. per lb., at present an ounce costs 2 s., and 1 lb. costs 23 s. 6 d[4]).

The trees in the botanical garden of the Faculty at Algiers which have been raised since 1913 from the seeds of the *Camphora officinalis*, Steud, similar to *Cinnamomum*

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[1]) *Drug. and Chemical Markets* 6 (1920), 343. — [2]) *Chemist and Druggist* 92 (1920), 219. — [3]) *Times Trade Supplement*, April 10th 1920. As per *Chem. and metallurg. Engineering* 22 (1920), 1030. — [4]) *Chem. Industry* 43 (1920), 309. These figures are only valid for the time when the announcement was published. As we remarked on page 9 of this *Report*, the value of camphor has sunk considerably during the last few months.

Camphora, Nees and Ebermayer, contained according to L. Musso[1]) well developed examples, yielding 1.1 per cent. of essential oil and from 1 to 1.1 per cent. of camphor. The seeds came from Formosa. On the contrary there was no camphor present in the trees raised in Algiers from hybrids, as *Camphora inuncta*, Nees[2]).

For the attainment of a successful culture, P. Carmody recommends the employment of seeds or seedlings from plants which yield solid camphor only[3]). Loamy ground should be avoided. Not more that 300 trees should stand on an acre. The trees can be cut for their camphor from three to four times annually when they have attained the age of 4 or 5 years.

According to another communication[4]) leaves and twigs can be cut from the two year old trees, at certain seasons, during which the growth ceases, without damaging then. This operation must be conducted with great care, and care must also be taken not to cut off the older branches. Only the leaves of the tree contain considerable quantities of camphor in its early years; and the branches which are then amputated only increase the raw material, but not the yield of camphor. With wages so high, the cutting by hand of the camphor tree has become so costly, that a profitable production of camphor in the Gulf States of America was endangered. For this reason, already in 1916 on the camphor plantation of the Satsuma Heights, Florida, attempts had been made to replace the hand labour by machinery.

The camphor trimming machine, built and latterly improved by the United States Department of Agriculture, consists of a wagon which carries the machine proper. The various parts which cut the leaves and twigs and assemble them on the wagon, are motor-driven. This machine, which can be worked by from two to three men, appears to come up to expectations.

Caraway Oil.—According to announcements of the Dutch ministry of agriculture the amount of land under caraway cultivation is 971 hectares this year, *i. e.* an increase of more than 50 per cent. over that in cultivation in 1919.

The high prices of the previous year, as was to be forseen, could not be maintained, during the last nine months they have gradually sunk to 19 fl. per 50 kilos, and appear for the time being to keep at this level. The satisfactory harvest and the considerable augmentation in the culture are factors which lead one to expect a further weakening in the prices in the next few months, especially if the slackness of trade which recently set in continues. At present caraway offers little inducement to speculation. Little demand is to be expected from Germany in view of the falling of the mark; especially as the new monopoly law and the spirit shortage greatly hinder the manufacture of caraway into spirits and liqueurs. Since the caraway-growing districts of Schleswig have fallen to Denmark, the German production may hardly suffice to satisfy the demand for seasoning purposes, so that large quantities of German caraway are not available for distillation.

Cassia Oil.—The export of cassia oil from Hong Kong for the year 1919 has further diminished[5]). The total value of this export for 1919 was $ 370792, and for 1918 $ 434245. In 1919 15 per cent. went to Great Britain and 72 per cent. to the United States[6]).

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[1]) *Bull. Sciences pharmacol.* **26** (1919), 204. As per *Pharm. Zentralh*, **61** (1920), 273. — [2]) Cf. *Report* April **1908**, 23. — [3]) *Times Trade Supplement*, April 10th **1920**. — [4]) *Perfum. Record* **11** (1920), 226. — [5]) *Drug. and Chem. Markets* **6** (1920), 789. — [6]) Cf. *Report* **1919**, 15.

As is known, small quantities of lead are always present in crude cassia oil, for the free cinnamic acid which this oil always contains attacks slightly the lead of the vessels in which the oil is forwarded[1]). F. Lubatti has devised the following colorimetric estimation method in order to determine the quantity of lead rapidly and simply[2]). 5 cc. cassia oil are diluted with 20 cc. of 90 per cent. alcohol. 5 cc. or 2.5 cc. of this solution, according as the lead content is greater or less than 0.025 per cent., are transferred to a 50 cc. Nessler-glass with small cavity (2.5 cc.) made up to 20 cc. with 90 per cent. alcohol. A test of lead-free cassia oil, obtained by distillation, is treated in a similar manner. Both liquids are treated with 1 cc. ammonium sulphide solution respectively. Then to the lead-free liquid is added such a quantity of alcoholic lead solution (1 cc. contains 0.0001 gr. lead), till the brown colours of the two liquids match. The lead-content is calculated from the formula $x = \frac{n \times 0.04}{m}$, where x = percentage content of lead, n = number of cc. of the lead solution used, and m = amount of the original solution.

The colours of the solutions can be matched by placing the Nessler glasses on a white enamelled tile and looking through them. However, either with aid of Dubosc's colorimeter, or with the apparatus described in the original paper, more exact results can be obtained. Generally the results are a little too high, but still within the limits of experimental error.

By a series of experiments it was established that cassia oil can take up in the course of a month as much as 0.074 per cent. of lead; a further increase in the lead content for longer periods was not observed. The commercial oil contains as a rule 0.04 to 0.06 per cent. lead.

Cedar-wood Oil, East African. — From the fresh wood-shavings of *Juniperus procera*, Hochst., of a pinacea from Nairobi (British East-Africa). 2 per cent. of an oil with an odour of cedar-wood was obtained by steam distillation[3]), that had the following properties: — $d_{15.3°}$ 0.987, $\alpha_{D20°}$ — 16°, $n_{D25°}$ 1.480. The oil was miscible with 90 per cent. alcohol in all proportions, and soluble in 70 per cent. alcohol in the proportion of 1 : 60. The amount of cedar camphor present in the oil was variable, according as the oil was distilled at once from the fresh shavings, or later. Shavings that had been exposed to the sun's rays for several weeks yielded practically only cedar camphor on distillation. An oil distilled immediately, as was the case which the one examined, contained only 38 per cent. of cedar camphor, which was isolated as long white needle-shaped crystals of melting point 75.5°.

Years ago Schimmel & Co. were able to obtain from East African cedar-wood. 3.2 per cent. of an oil, which was semi-solid at ordinary temperatures, and from which cedar camphor of melting point 86 to 87° was obtained[4]).

Chamomile Oil. — We have been unable to purchase large consignments of flowers suitable for distillation this year on account of transport difficulties in Hungary; and since the native lots, which are occasionally offered us give a very poor yield of oil, a temporary shortage of this commodity must still be reckoned with.

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[1]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 431; cf. also *Report* **1916**, 12. — [2]) *Journ. Soc. chem. Ind.* **39** (1920), T. 35. — [3]) *Journ. Soc. chem. Industry* **38** (1919), T. 364. — [4]) Cf. *Report* October **1911**, 106.

Oil of Chrysanthemum marginatum. — Y. Shinosaki obtained, by means of steam distillation, from *Chrysanthemum marginatum*, Mig., a composita known in Japan as *Isokiku*, 0.005 per cent. of a greenish-blue oil with following characteristics: d_{15° 0.9231, $[\alpha]$ — 46.58°, n_{D20° 1.5020, saponification value 16.30, ester value after acetylation 63.09. In addition to esters and alcohols, small quantities of an aldehyde or ketone were present which gave a crystalline bisulphite compound[1]).

Cinnamon Oil, Ceylon. — According to an announcement of the *Weekly Times of Ceylon*[2]) the shortage of Ceylon cinnamon is caused by the planters growing coconuts and caoutchouc instead. There is little prospect of the cultivation again increasing. The wild cinnamon trees in the jungles and forests, formerly exploited, have been mostly destroyed by the clearings. The cinnamon crop of 1919 was especially small on account of unfavourable weather; the prospects of the 1920 harvest are better, since rain fell at the right time.

Four different places on the Gold-Coast, Tarquah, Assuantsi, Coomassie and Aburi (Agricultural Stations) forwarded cinnamon bark to the London Imperial Institute, the essential oils of which were distilled and examined there[3]). We have already reported on the oil coming from Tarquah[4]). For comparison the results also of this investigation are given once more.

Cinnamon bark from:	Assuantsi	Coomassie	Aburi	Tarquah
Heavy oil	1.5 per cent.	1.6 per cent.	1.4 per cent.	1.18 per cent.
Light oil[5])	0.3 „ „	0.4 „ „	0.3 „ „	0.3 „ „
Total oil:	1.8 per cent.	2.0 per cent.	1.7 per cent.	1.48 per cent.

The heavy oils had an especially pleasant odour; not only the oil-yield but also the aldehyde content of the oils was very high, as is seen from following table:—

Heavy cinnamon oil from:	Assuantsi	Coomassie	Aburi	Tarquah
$d^{15^\circ}_{15^\circ}$	1.038	1.042	1.041	1.042
n_D	1.594	1.606	1.603	1.603
Aldehyde content (approximate)	74 per cent.	88 per cent.	86 per cent.	86 per cent.
Solubility in 70 per cent. alcohol in	2.5 parts	2.4 parts	2.4 parts	2.4 parts

A cinnamon bark oil from Ceylon, and obtained by us via London, was sampled, and proved to us that the bad habit is still followed there of distilling the bark and the leaves together[6]) so that naturally no pure bark oil is obtained. Such distillates are recognised, apart from their different smell, most of all by the too low aldehyde content and the too high eugenol content. We let the constants of the sample follow, and give simultaneously the valid limiting values for Ceylon cinnamon-bark and cinnamon-leaf oils, which brings out in the best manner, the extent to which the oil is rendered impure by the presence of the leaf oil: —

	Sample	Bark oil	Leaf oil
d_{15°	1.0445	1.023 to 1.040	1.044 to 1.065
α_D	— 0° 28′	slightly left, as a rule not over — 1°	— 0° 15′ to + 2° 20′
Aldehyde content	29 per cent.	65 to 76 per cent.	up to 2.5 per cent.
Phenol content	50 per cent.	4 to 10 per cent.	65 to 95 per cent.
Solubility in 70 per cent. alcohol	sol. in 1.7 vols., and over	sol. in 2 to 3 vols.	sol. in 1 to 3 vols.

[1]) *Journ. Chem. Ind. Tokyo* **22** (1919), 455. According to *Journ. Soc. Chem. Industry* **38** (1919), A. 877. — [2]) *Ind. u. Handelsztg.* **1920**, No. 9. — [3]) *Bull. Imp. Inst.* **17** (1919), 189. — [4]) Cf. *Report* **1919**, 18. — [5]) Obtained by extracting the distillation water with ether. — [6]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 418.

According to this the cinnamon leaf content of the sample exceeds 50 per cent., and it is quite understandable that such a mixture is useless as cinnamon-bark oil.

Another sample from Paris contained no cinnamon bark oil whatever, but consisted solely of leaf oil ($d_{15°}$ 1.0455, $\alpha_D \pm 0°$; 75 per cent. eugenol, soluble in 1.4 vols. 70 per cent. alcohol); and two further samples from Hamburg apparently consisted solely of cassia oil. The smell alone decided its uselessness!

Oil from the (Trunk) Bark of Cinnamomum pendunculatum.—According to an announcement of Raspe & Co. (Kobe)[1]) an essential oil of the trunk bark of *Cinnamomum pendunculatum*, Nees. had an angle of rotation $\alpha_D + 28.54°$. Keimazu and Asahina[2]) observed with such an oil a rotation to the left ($[\alpha]_D - 280.54'$ [$-4°40'$?]); and we also, with a sample sent to us from Japan, observed an optical rotation of $\alpha_D - 14°32'$[3]).

Oil from the Leaves of Cinnamomum pendunculatum.—In the same communication[1]) the following data were given *re* the essential oil obtained from the dry leaves of *Cinnamomum pendunculatum*, Nees. The dried drug yielded, according to S. Tsuguchi[4]) 1.4 per cent. essential oil, equal to 0.7 per cent. of fresh leaves used ($d_{15°}$ 1.0722; boiling point 190 to 245°). This oil contained *iso*eugenol and at 8° separated out stearoptene.

According to an investigation of Y. Shinosaki[1]) 80 per cent. distilled over at 230 to 240° under ordinary pressure. On cooling to as low a temperature as —20° no crystals separated out. The alcoholic solution gave a bluish-green coloration with ferric chloride solution, and scarcely any crystal formation on being staken up with sodium bisulphite solution. The angle of rotation is $\alpha_D + 1.75°$, not $\alpha_D - 1.75°$, as stated in *Perfum. Record* 7 (1916), 64[5]).

Citronella Oil.—During recent years the following quantities of citronella oil were exported from Ceylon[6]):—

1916	1917	1918	1919
1 350 002 lbs.	1 211 197 lbs.	1 048 202 lbs.	1 050 989 lbs.

Distributed as follows:—

	1919	1918
Great Britain	336701 lbs.	275217 lbs.
Belgium	3714 „	—
France	145750 „	4421 „
Holland	31528 „	—
Italy	23321 „	—
Australia	39964 „	80531 „
U. S. A.	377940 „	439323 „
Egypt	—	9211 „
Africa	2582 „	1188 „
India	62379 „	51974 „
China	24108 „	44718 „
Japan	598 „	94236 „
Other Asiatic countries	3404 „	1324 „

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[1]) Publications by Y. Shinosaki, *Report of the Industrial Laboratory (Kogyo Shikenjio)* Tokio, March 1916. *Yakugaku Zashi* 1906, 1095. — [2]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II. p. 446. — [3]) *Ibidem* October 1907, 34. — [4]) *Ringyo Shikenjio Report* No. 5 (The year number is missing). — [5]) Cf. also *Report* 1916, 14. — [6]) *Perfum. Record* 11 (1920), 27.

The export of Citronella Oil from Java and Madura was: —

1913	1914	1917	1918	1919
75.2 t.	136.6 t.	515.7 t.	228.0 t.	528.5 t.

Whilst the exports of 1913 chiefly went to the Netherlands, Germany and France, those of 1917 went above all to England, America and Japan. However in 1918, only America and Japan remained as the chief countries to which this commodity was exported[1]).

Exported to: —	1917	1918	1919
Holland	5.5 t.	—	233 t.
France	15.5 „	—	69 „
England	213.6 „	—	91 „
America	205 „	84.4 t.	85.6 „
Japan	50 „	80.8 „	7 „

Citronella Oil, Burmese. — Since 1912 citronella grass (*Andropogon Nardus*, Linn.) had begun to be cultivated in Burma in the neighbourhood of Moulmein and Amherst, with good success, and turned to profitable account for the obtaining of citronella oil. Burma citronella Oil, containing from 82 to 94.7 per cent. total geraniol (geraniol + citronellal), was recognized in 1914 in the London market as being as good a product as Java oil. The new industry developed well in spite of the war and promises to become profitable[3]).

Clove Oil. — A total of 824501 frasilas (1 frasila = 35 lbs.) of spice cloves were harvested in 1919 in the islands of Zanzibar and Pemba, of which Pemba produced 565229 frasilas and Zanzibar 259272 frasilas[3]).

According to a report distillation works are in the course of erection on the islands of Zanzibar and Pemba for the winning of oil of cloves. The undertaking is supported by the authorities[4]).

Essential Oils, Sicilian and Calabrian.

Our friend, Herr Eduardo Jacob, German Consul in Messina before the War, who returned home early in the year, has given us a comprehensive report of the essential oil market, which we give verbatim to our readers.

It is our sorrowful duty to announce that the above-named gentleman died suddenly shortly after the completion of his report. This news will be received with the deepest sympathy in all branches of the essence trade. All those who were interested in purging the Sicilian and Calabrian trade in essences, of its irregularities and adulterations owe him an immense debt of gratitude; more especially so as they have enjoyed the advantages of this purification. Herr Jacob was the first in the essence trade to place himself enthusiastically in the service of the good cause, when, more than 30 years ago, we proceeded against the prevalent adulteration mania, by the working out of trustworthy methods of examination. Although lacking in a scientific education, he developed in the shortest time such a skill and exactitude in conducting investigation pro-

[1]) *Handelsberichten* (Den Haag) **14** (1920), 184. — [2]) *Chemist and Druggist* **91** (1919), 815; *Chem. Ztg.* **44** (1920), 38. — [3]) *Ind. und Hand.-Ztg.* No. **148** (1920), 1002. — [4]) *Perfum. Record* **11** (1920), 91.

cesses, that was astonishing, and he soon become so proficient that he was recognized in the producing circles as the first authority in the knowledge of the conditions. Soon other Messina and Calabrian firms followed his example, so that in a few years a complete revolution in the essence trade in favour of honest dealing was effected. For his whole-hearted participation in the fight against the adulteration scandals, in which he experienced many a disappointment and made many an enemy, the thanks of all the other participators are due to him, and it would be unpardonable if we did not mention here yet again his loyal cooperation. His reports, which testified to his excellent expert knowledge, upon which he grudged neither time nor effort, and which were always readily placed at our disposal, will henceforth he sadly missed by our readers.

I. The Essence Market during the World War.

When the World War broke out in early August 1914, there were quite important stocks of essential oils of the citrus group in Sicily and Calabria; for the recent harvests there had, on the whole, been very satisfactory, and the manufacture of the various oils had yielded thoroughly good results.

Moreover the foreign demands during the first seven months of the year 1914 had been rather weak, and the outbreak of the World War at first caused an almost complete suspension of general traffic conditions.

This also nearly completely crippled the export for the remaining months of 1914; the shipments to North America which at that time were still possible, as well as the dispatches by rail to the countries of Central and Northern Europe, solely and alone maintained a weak commercial connection between South Italy and abroad.

Consequently it is not to be wondered at, that the Sicilian and Calabrian essence market during the last quarter of 1914 become a continually sinking one.

The extraordinarily low price level of the South Italian and Sicilian essential oils first attracted foreign demands at the beginning of 1915, in spite of the difficulties of shipment, which had greatly increased in the meanwhile. Germany especially, who saw the threatening Italian war clouds gathering against her on the horizon, hastened to renew her store in as great a degree as possible before the storm broke.

A brisk export set in in the new year, which not only stopped the sinking of the prices, but also evoked an improvement in the value of essences of all kinds.

The entry of Italy into the war in May 1915 barred the export of the Italian essential oils to the important consuming countries Germany and Austria-Hungary; the disappearance of these two markets, and the ever-growing danger of the over-sea traffic meant a time of heavy trade depression for these products, which continued throughout the war.

Manifold attempts of local groups of speculators during the years 1915 to 1918 caused, here and there, greater or smaller fluctuations of a temporary nature, in the price of this or that essence; but always in the end the burden of the large and ever-increasing stocks, especially those of the leading lemon oil, again bore the prices down.

The increasing difficulties of over-sea transport prevented the exportation of the fresh fruits in cases. Germany and Austria had ceased to be customers, so that South Italy was deprived of the greater part of her important fruit exports. The oranges indeed were destined for the Italian army and the allied troops; but the enormous quantities of lemons in the country, otherwise unusable, fell to the oil manufacture, and the therewith connected production of calcium citrate.

With the low prices of oil, this manufacture was practically devoid of profit; however, the manufacturers were richly compensated for this by the ever rising prices of the bye-product — calcium citrate, the crude material for crystallised citric acid.

During the war-period the total exports of essential oils from South Italy were as follows: —

1914	708 952 kg.,	worth	14 184 516	Lire
1915	921 867 „	„	13 873 435	„
1916	911 362 „	„	15 735 132	„
1917	732 451 „	„	17 202 686	„
1918	875 439 „	„	26 161 083	„

The greatly enhanced value of the export for 1918 is to be traced to the raising of the value of all kinds of essential oils, which in its turn, is due to the greatly increased costs of production.

The figures you give on pages 25 and 26 of your *Report* April-October 1919 of the export of essences for the year 1918 are obviously incorrect. Your guarantor has apparently omitted to convert into kilogrammes, the quantities which lay before him as Sicilian pounds and has multiplied the official average price per kilogramme by the Sicilian pound, from which quite fantastic figures have resulted.

The more correct figures are as follows: —

Oil of Bitter Oranges . . .	kg.	98 680	= Lire 35.—	Lire	3 453 800
Oil of Bergamot	„	259 244	= „ 65.—	„	16 850 860
Oil of Lemon	„	514 113	= „ 11.—	„	5 655 243
Oil of Mandarin	„	2 162	= „ 70.—	„	151 340
Other Oils	„	1 240	= „ 40.—	„	49 840
	kg.	875 439	Lire	Lire	26 161 083

For the sake of a clearer exposition of the price course a table is added to the attached paper (*i. e.*, 2nd column of figures given above — Lire 35, &c.) which contains the average monthly market sale prices for the period June 1914 to June 1920 in the Italian lire standard and for a Sicilian pound of 317 grammes. For the time of the rise in the first half of 1920 separated average figures for each half month are shown. (See p. 21.)

The price fluctuations noticeable in this table will be spoken of later in the discussions over the fate of each individual kind of essence.

In the past year, 1919, the export of essences from South Italy amounted to 1 266 108 kg.; a table of values is not yet possible, since the official publications in regard thereto have not yet arrived.

The customary pre-war distribution of South Italian essential oils amongst the various consuming countries has undergone a radical displacement by reason of the war. Many countries formerly importing small quantities only, suddenly received an increased significance for this market, for example — Holland, Switzerland, Denmark, and Scandinavia.

Now, as formerly, the United States of North America take the greater share of the South Italian essences, then come England and her colonies.

North America took annually more than half of the total export, *viz.*: —

1915	1916	1917	1918	1919
326 348 kg.	373 183 kg.	431 309 kg.	402 301 kg.	534 158 kg.

Monthly Average Prices of Sicilian & Calabrian Essences during the years 1914 to 1920.

Prices quoted in Italian[1]) Lire per Sicilian Pound of 317 grammes.

Year	Month	Lemon Oil	Bergamot Oil	Sweet Orange Oil	Bitter Orange Oil	Mandarin Oil
1914	June	6.—	13.50	6.—	4.50	14.60
„	July	5.25	13.25	5.90	4.30	15.—
„	August	4.60	12.40	5.75	4.25	15.—
„	September	4.05	11.50	5.—	4.15	14.50
„	October	2.70	9.50	3.70	4.—	11.—
„	November	2.65	8.50	3.95	4.—	9.—
„	December	2.25	8.05	3.80	4.—	9.—
1915	January	2.65	7.70	3.90	4.—	9.—
„	February	2.70	7.55	4.—	4.—	9.30
„	March	2.40	7.25	3.90	3.75	11.25
„	April	2.50	8.15	4.65	3.65	14.25
„	May	2.60	8.75	4.90	4.—	16.—
„	June	3.05	8.80	5.50	4.25	19.—
„	July	4.—	10.70	6.65	5.15	21.50
„	August	3.20	11.40	5.55	5.—	22.—
„	September	2.85	10.50	4.90	4.—	22.—
„	October	2.60	9.70	5.35	4.25	16.50
„	November	2.45	9.70	5.—	4.90	18.75
„	December	2.75	9.90	6.05	5.50	15.—
1916	January	2.55	9.95	6.65	5.75	20.50
„	February	2.50	9.80	6.95	6.25	25.—
„	March	2.65	11.—	7.30	6.75	25.25
„	April	2.75	13.20	9.70	9.10	27.50
„	May	2.45	12.80	9.70	9.40	27.—
„	June	2.50	12.70	8.70	9.05	25.—
„	July	2.60	15.50	9.60	9.—	25.—
„	August	2.60	21.50	9.70	9.—	25.—
„	September	2.65	20.80	8.70	8.50	25.—
„	October	2.70	19.30	7.80	8.—	22.75
„	November	3.05	16.50	9.45	10.25	21.75
„	December	3.30	16.20	9.75	11.50	22.—
1917	January	4.05	17.20	10.10	11.70	22.—
„	February	3.65	17.10	9.70	11.40	22.—
„	March	3.25	17.—	9.10	10.40	22.—
„	April	3.—	19.—	8.90	10.—	21.50
„	May	3.—	19.—	9.65	10.50	22.25
„	June	3.05	20.30	10.15	11.—	24.50

[1]) A lira is normally equivalent to a franc.

Year	Month	Lemon Oil	Bergamot Oil	Sweet Orange Oil	Bitter Orange Oil	Mandarin Oil
1917	July	3.15	22.—	10.—	11.—	25.—
„	August	3.—	20.25	9.70	11.—	25.—
„	September	3.—	19.35	9.20	9.60	25.—
„	October	3.—	19.—	9.20	9.50	24.50
„	November	3.20	21.—	9.40	9.50	24.—
„	December	3.—	21.35	9.80	9.50	24.—
1918	January	2.45	20.50	9.60	9.50	23.75
„	February	2.75	19.90	9.10	8.25	21.—
„	March	2.80	20.10	9.10	8.10	21.—
„	April	2.80	20.25	8.95	8.—	19.75
„	May	3.—	20.30	9.—	7.80	19.25
„	June	3.20	20.25	9.20	8.—	20.50
„	July	3.25	20.20	9.—	7.85	19.50
„	August	3.35	20.25	9.—	7.90	19.—
„	September	3.40	20.15	8.90	7.75	18.25
„	October	3.50	20.10	8.85	7.65	17.75
„	November	4.20	21.40	9.35	8.15	18.20
„	December	5.60	23.20	10.25	10.05	19.25
1919	January	4.—	22.05	10.85	10.10	19.25
„	February	3.80	20.15	10.30	9.25	20.—
„	March	3.60	20.25	10.55	9.25	20.—
„	April	3.60	20.25	10.40	9.35	23.50
„	May	4.—	20.25	10.85	12.—	31.—
„	June	4.05	20.20	13.30	15.50	42.50
„	July	4.45	20.25	13.90	17.30	58.—
„	August	5.—	20.80	16.10	19.25	76.—
„	September	4.95	21.20	16.45	20.50	80.—
„	October	6.55	23.—	20.—	25.50	83.50
„	November	8.80	29.10	28.35	27.75	92.—
„	December	10.40	30.20	35.50	36.—	85.—
1920	1st to 15th January	13.15	36.75	48.50	47.—	85.—
„	16th „ 31st „	14.80	42.25	47.40	47.—	86.50
„	1st „ 15th February	15.60	46.50	52.40	44.—	93.—
„	16th „ 29th „	16.50	53.25	75.50	47.85	102.—
„	1st „ 15th March	21.50	74.40	97.50	56.—	125.—
„	16th „ 31st „	24.75	93.—	138.—	67.—	142.—
„	1st „ 15th April	24.—	93.50	163.—	78.—	165.—
„	16th „ 30th „	23.50	93.—	180.—	85.—	197.—
„	1st „ 15th May	21.—	93.—	184.—	90.—	195.—
„	16th „ 31st „	20.—	91.75	155.—	80.—	185.—
„	1st „ 15th June	16.—	84.—	115.—	61.—	161.—
„	16th „ 30th „	13.—	79.50	86.50	48.—	147.—

In 1919 the exports from South Italy to German ports amounted to only 17850 kg.; whilst Switzerland took 11350 kg., and 18296 kg. were shipped to Holland. It may be assumed that a great part of the exports to Switzerland and Holland has found its way from there to Germany.

The foregoing general remarks would be incomplete if we did not mention the wild forcing up of prices of all kinds of essences, which began about November 1919 and toward the end of May of this year collapsed ignominiously, as it well deserved to.

The prices of the sweet oil of orange made the beginning, and in a few weeks were forced up from 20 lire — for the Sicilian pound of 317 grammes, — to 45 lire.

Although several weighty reasons existed for the price-raising of this oil, the elevation is to be ascribed for the most part to the machinations of a strong group of speculators furnished with sufficient money. Emboldened by this first successful speculation, which caught the export firms unprepared and caused them heavy losses, since the greater part of them had sold on delivery and at cheap prices orange oil abroad, the speculators blindly rushed to other oils; first to the more easily cornered oil of bergamot, and then to lemon oil which offered more difficulties to their manipulations on account of the great supplies.

The export firms taken by surprise all along the line, and driven into a corner, were obliged to cover with heavy losses their uncovered sales on delivery abroad. — However, this upward movement of all prices would not have continued for such a time, and would have been unable to have assumed such proportions, if the simultaneous lowering of the Italian money standard, on account of a very strong rise in the foreign exchange had not come to their help; which guaranteed the comparative cheapness of the South Italian oils for abroad, in spite of the high prices, as long as these had not grown infinitely high. This rendered the dispatch of profit bearing consignments to America for quite a time, where they found a brisk market.

Under those circumstances the pushing up of the prices was continued until they became fantastic, so that finally oil of bergamot cost 100 lire, sweet orange oil 180 lire, and lemon oil 25 lire per Sicilian pound (of 317 grammes) respectively.

No higher rate of exchange could compete with such insane rises in prices; the consignments abroad ceased; the consuming countries stopped ordering, and trade came to a standstill for several months, till at last the speculators bowed to the force of circumstances, and sought to save what was yet saveable.

This sealed the fate of price-forcing; the artfully built edifice of excessively forced up prices crumbled together in May, and in June and July of this year prices fell to a lower level, *e. g.*

Oil of Bergamot . . .	fell from	100	lire	to	70	lire
Sweet Orange Oil . . .	„ „	180	„	„	60	„
Lemon Oil	„ „	25	„	„	12	„

with which the local speculative mania came temporarily to an end.

Re the detailed discussion of the fates of the individual essences during the last five years we first turn our attention to

Bergamot Oil. — Already before the world war the fact was known to the initiated, that after the earthquake of 1908, which visited Messina and the southern extremity of Calabria, the yearly bergamot oil harvest would no longer be sufficient for the world demand.

Thousands upon thousands of bergamot trees had to be felled to make room for the barrack camps to supply the place of the villages destroyed by that terrible earthquake; at about the same time a new disease of the *Citrus* trees appeared, which damaged the tenderer bergamot tree more than its more-resisting cousins, and unfortunately caused the death of a large quantity of bergamot trees.

Against the aforesaid lowered power production of South Calabria, an ever-increasing world consumption developed abroad.

This announces itself quite clearly in the steady and continuous rise in the price of this oil during the last 12 years.

The result of these conditions is that moderate or bad harvests have a greater influence over the price of oil of bergamot for the time being than is the case with lemon oil for example.

In the autumn of 1914 oil of bergamot cost 13 lire — per Sicilian pound of 317 grammes. The slackness in trade which happened in the later months of the year, as well as the good results of the new period recovery, which was just commencing, caused the price of bergamot oil to slowly sink to 7 lire; towards the end of April 1915 a turn took place which brought the value of the oil up to 11.50 lire during the summer.

For a short time there was a reaction followed by a repeated tightening of the prices for in addition the rather poor harvest predicted had been damaged by the summer heat.

Since then, from 1919 to May 1920 the price of bergamot oil has been mainly on the up grade.

Standing at 22 lire in August 1916, the oil fell to 17 lire during the production season January to March 1917, but rose again in the following July to 21 lire and kept at this level right into December 1918.

The harvest period of the winter 1918/1919 caused the price to sink by one or two lire, and it was maintained at this level until, in the late autumn of 1919, the local speculation made itself master of the bergamot oil and drove the prices up without any just reason.

In November 1919 the oil stood at 28 lire, in December at 35 lire, in January 43 lire; February 53 lire, March 90 lire, and in April the price rose to 100 lire.

Bergamot oil, like the other oils, suffered a fall in price, only in a lesser degree, in May and stood at 70 lire; during the lest few months the price has recovered somewhat and now stands at 80 lire.

Re bergamot harvest of 1920, see page 27 of this Report.

Re export of bergamot oil from Italy, see page 30 of this Report.

Lemon Oil. — The prices of this oil have rise and sunk during the course of the war, *i. e.*, right into the late autumn of 1918, generally throughout the whole period the variations were moderate and the price increase or decrease seldom attained 50 %.

Such price variations were generally of short duration, since they were caused almost exclusively by local speculation, with the idea of effecting a rise in the price of the fresh lemons on account of the rise in price of the oil.

Lemon oil stood at 2.25 lire per Sicilian pound of 317 grammes in January 1915; it reached its highest price of 4.75 lire in June, and fell, after Italy's entry into the world war, to 2.50 lire towards the end of September.

In 1916 the price of lemon oil was maintained with difficulty, and was only increased to 3.50 lire towards the end of the year.

The harvest season 1916/17 had to contend against difficulties of production on account of the scarcity of labour, nevertheless the yields remained about the same, and there were no remarkable variations in price during the year 1917, indeed a renewed advance in local speculation was necessary in order to maintain the oil at the average price level of 3 lire.

The stocks of this oil had continually increased in the course of the year, and the prospects of a further increase owing to the good harvest of the winter 1917/1918 brought down the price to 2.20 lire in spite of all efforts to the contrary.

A prolongation of such unsatisfactory conditions threatened seriously the interests of further agricultural circles, as well as the numerous classes of people who gained their living in the lemon trade and lemon raising.

As usual, the Government was bombarded with requests for help and protection. A lucky chance gave it the opportunity of helping itself in helping the agriculture and industry of southern Italy.

A very serious scarcity of oil of turpentine had arisen in Italy during the War. Already in 1917 official attempts had been made to substitute lemon oil for oil of turpentine; these experiments turned ont satisfactorily.

Hence, on account of the crying needs of all Government workshops, arsenals, shipbuilding yards for oil of turpentine, a law was proclaimed appointing a Government commission with orders to supply the state with 300000 kilos lemon oil from manufacturers and traders, and to further the home consumption of lemon oil as a substitute for oil of turpentine.

The price fixed for this compulsory sale amounted to only 2.64 lire per Sicilian pound of 317 grammes; yet it relieved the pressure in lessening the stocks, which exerted an influence an the price.

The example of the Government was naturally followed in private industry, so that altogether very considerable quantities of lemon oil were used up in their own country.

This measure combined with the inflowing orders from all countries for this oil, after the conclusion of the armistice led to a great demand, and in the last two months of the year the price of lemon oil we from 3.50 to 6 lire; only to sink again towards the end of January 1919 to 3.75 lire.

An exceptionally rich production during the first four months of 1919 kept the price of the oil at this level till May, in spite of the greater demands of the market on account of the reviving exports.

Lemon oil commenced to soar in price from the middle of May onwards; the demands from abroad, and the consequent desire for speculation of the markets would not allow the price to steady itself.

Capital, which during the War had otherwise been profitably invested, became free, and was at once invested in the local essential oils.

Money so easily earned during the War was recklessly gambled with; the first success intoxicated; till finally wider and wider circles of capitalists were seized with the fever of speculation, in which common sense was cast to the winds; and without cause or reason the prices of all oils soared to crazy heights.

From June to December lemon oil rose each month on an average by 1 lira per pound; till under the continual lowering of the Italian standard and the consequential raising of the rate of exchange, it rapidly rose from December 1919 to April 1920 to the unheard-of height of 25 lire.

The prudent and practical behaviour of foreign countries as well as a fall in the rate of exchange put a sudden end to the crazy doings of the local speculation circles.

Already in the beginning of April these top prices were maintained wich difficulty, they then began to fall, slowly at first, and then rapidly, until the price of lemon oil stood at 12 lire.

Re lemon harvest for 1920, see p. 28 of this *Report*.

Re information about adulteration of lemon oil, see p. 31 of this *Report*.

Mandarin Oil plays a more important rôle in the essence trade during recent years than it formerly did, and is bought up each year by foreign countries to the last drop; hence it is an excellent commodity for purposes of speculation.

We find that this oil sinks in price during the production period, but as soon as this is over it rises to higher prices for the rest of the year, until the succeeding harvest again induces a temporary fall.

The increased consumption of this oil has been accompanied by an increase in price.

When Italy entered the World War the price of orange oil was 10 lire, but in the same year it reached 22 lire.

Throughout 1916 and 1917 the price varied between 22 and 25 lire; in 1918 up to April 1919 a slight weakening in price took place — lowest 17 lire, highest 21 lire.

From May 1919 onward, the value of mandarin oil rose more and more rapidly — May 1919, 30 lire; July, 58 lire; October, 80 lire; December, 90 lire; January 1920, 95 lire; February, 100 lire; March, 135 lire; April, 170 lire; May, 200 lire.

The lowering of the market prices which set in in May of this year did not affect orange oil, for at that time it was completely sold ont.

Re mandarin harvest of 1920, see p. 28 of this *Report*.

Re adulteration of mandarin oil, see p. 32 of this *Report*.

Oil of Bitter Oranges has varied in price to a far less degree than the sweet variety.

At the beginning of 1915 its highest value stood at 4 lire, and remained so throughout the year.

During the first quarter of 1916 the price was raised to 9 lire, and with slight variations kept at this level till middle of November.

The price remained at 10 lire throughout the year 1917:—till, in January 1918, a sinking of two lire took place. Soaring above the price of the sweet orange oil, the oil of bitter orange rose to 26 lire in November 1919. During the great speculation period November 1919 to May 1920, the price was rapidly screwed up from 30 to 90 lire. No prices higher than this were paid; and in the universal fall of prices it sank to 45 lire.

Orange Oil, sweet. — The oil prepared in South Italy had for many year before the war not sufficed for the world consumption, this deficit was partly made good by Cuba which delivered ever increasing quantities of a lower grade, but cheaper oil.

Hence it is not astonishing that South Italy can yearly dispose of its total quantity of orange oil abroad, and that only a very insignificant quantity is carried over from one harvest to the next.

Whilst lemon oil and orange oil generally stood at almost the same price level in former times, yet recently this relation has changed in favour of the orange oil, which has acquired a higher value.

The market price of orange oil at the outbreak of the World War was 6 lire per Sicilian pound of 317 gr.

The quietness of trade in the last quarter of 1914 caused a temporary weakening of the price which fell to 5 lire, but in January 1915 the already mentioned livelier export set in, through which the value of the oil was at once raised, so that in May 1915 it reached the respectable level of 10 lire.

This price, with slight variations towards a fall, continued right into the commencement of the new production.

When the new oil made its appearence, the price sank temporarily to 7.50 lire, but already in November it went up again to 10 lire, and kept at this level throughout 1917 and right into December 1918.

The poor orange harvest of 1918/1919, and the increased demand from abroad after the Armistice, occasioned a gradual increase of the price during the early months of 1919, and then from June on a rapid increase.

In May 1919, 11 lire; in June/July, 13 lire—14 lire; in August/Sept. 15 lire—16 lire were paid.

Unfortunately the harvest 1919/1920 turned ont to be only a poor average harvest; this condition, and the fact that in the meantime the anti-alcohol Act of North America had come into force, brought about completely new conditions for the disposal of the oil.

In the preparation of drinks, which should replace spirit, it turned out that as the basis of almost all new drinks, orange oil could be advantageously used. Hence this oil was demanded by America in large quantities, as has always been the case up to now.

The greater demands for orange oil could not escape the market speculations, which at once felt the presence of an attractive opportunity for speculating, and did not let it escape.

Hence in October 1919, a mad movement in the orange oil market commenced; the oil went up by leaps and bounds; in October, to 22 lire; November, 28 lire; December, 36 lire; January 1920, 48 lire; February, 64 lire; March, 118 lire; April, 172 lire; till in the first half of May it had reached its maximum price of 185 lire.

The inactive behaviour of the consuming countries abroad, the weakening rate of exchange, but most of all, the appearance of an extraordinarily rich blossoming of the orange trees, finally broke the thick-headed madness of the speculators in, and owners of, orange oil; the latter half of May already showed an average price of 155 lire; at the end of June it could be bought at 75 lire, and in the first half of July, the minimum price of 65 lire was reached.

Indeed this only continues a few days, for not inconsiderable covering purchases held back up till now by the local shippers, allows the price to run up to 90 lire — even 100 lire is paid for a small choice lot.

Firm sale prices for this oil from then onward have not existed; the supplies were extraordinarily diminished; and since then the prices have been ruled by the export requirements of the time, and the greater or lesser inclination of the smaller owners to sell.

In general the average price during the last months is given as 70 lire.

Re orange harvest in Italy for 1920, see p. 29 of this *Report*.

Re production of orange oil in the West Indies, see p. 32 of this *Report*.

Re an adulterated sweet orange oil, see p. 31 of this *Report*.

II. The Essence Market. Beginning of September 1920.

The most recent events, *i e.*, the forcing up of the prices of all essences to giddy heights by ignorant and unscrupulous manufacturers and speculators, has left behind amongst those who have been badly but financially in the local export circles, a deep feeling of uneasiness, and also great mistrust against the originators of the quite unjustified price raising, and has created an uncertainty, over the consequences of which one cannot at present, even with the best of wills, form an opinion. Unfortunately the speculators, although the fall in prices may have cost them much money, have cause to look back upon the result of their ventures with satisfaction.

As a matter of fact, they succeeded in November of last year to set the market in movement by surprise, and many an export house has had to suffer heavy losses on hastily uncovered sales abroad.

After the above experiences nobody will have any trust in carelessly uncovered deliveries of oil abroad in the immediate future.

The inclination of the speculators to influence the prices of essences also in the coming year, by the buying up and holding back of large quantities undoubtedly exists. The position is, however, not so favourable as last year in so far as the market for the coming harvest has no delivery obligations for abroad. The development of the trade will depend exclusively on the position which the foreign customers take up against a fresh rise in prices.

These considerations indeed will scarcely hold the reckless gambler back from repeated forcing up of the prices, but it can now be predicted with comparative certainty that fresh wanton attempts will be made to disturb the natural development of the market, but to a much smaller extent, and in a short time they will collapse.

The following announcements will be of use *re* the given prospects of the nature and conditions of the new business year, and the hopes of the new harvests.

Bergamot Oil. — This is the only citrus species whose blooms were not genuinely satisfactory this year and which only gave promise of a harvest slightly above the orange. Besides, the weather conditions during the summer have not been favourable for the development of the young fruit.

Apart from insufficient irrigation the fruits have suffered from the unusually high summer heat. The leaves of the bergamot trees are to-day hanging curled up by the heat and drought. Since, in this condition, they can offer the fruit no satisfactory protection against the scorching rays of the sun, the latter has been much damaged especially in the exposed spots on the lowland coast-strips.

No sure estimate can be made of the amount of bergamot oil at hand; but we shall not be far from wrong in assuming that there is still a certain amount in the hands of the obstinate land owner and the speculators who were caught napping when prices fell.

Both these parties have plenty of money at their disposal, and will defend their advantage with obstinacy.

Whether a result of the damage proved to have been suffered by the hanging crops, or whether at present there is no bergamot oil in the hands of those in need of money, it is a fact that at present this oil has a tendency to rise; in the last few days it has sold for 80 lire; and to-day, only a still higher price will persuade this or that owner to dispose of small lots of bergamot oil.

From the above it is seen that the price of bergamot oil in the course of next year will in all probability reach a high level.

Re bergamot harvest during recent years, see p. 23 of this *Report*.

Re export of bergamot oil, see p. 30 of this *Report*.

Lemon Oil. — The market at present has at its disposal considerable supplies, of the existence of which there is no doubt; but the quantity cannot be given in figures, since all the oil owners keep quiet about their supplies.

The hanging crops on the north coast of the island, according to all appearance, give promise of a plentiful harvest; the lands in the east of Sicily, however, appear to be less fortunate, yet in spite of this, a harvest slightly above the average is hoped for. The long-continued drought of nearly nine months alone occasions doubt.

The winter rainfalls were extremely insignificant, the springs yield only half their usual quantity of water this summer; and the height of the ground-water has sunk greatly.

Hence the watering of the trees has only been partial and consequently the growth of the lemons has been retarded. If the rain keeps off much longer the fruit may suffer from disease, and the yield of oil be reduced.

In judging the probable cost price of lemon oil of the new harvest we come to the following considerations.

The development of the social conditions of the new time has at least in Italy, kept pace with that of the rest of the civilised world; the results and influence of which on industry at last begin to make themselves felt and play a decisive rôle.

Here also wages have risen tremendously, and the hours of work been shortered; increased prices for coal, wood, metal; in short every expense with which the production of oil was hitherto burdened, and not least the increase in the fruit prices occasioned by the same conditions; all these make it impossible that the price of lemon oil will be able to sink to its pre-war level.

With present conditions, the opinion in producing circles is, that the net cost of lemon oil from the new crop will be hardly less than 10 lire per Sicilian pound of 317 grammes.

Re production of lemon oil during recent years, see p. 23 of this *Report*.

Re information over adulteration of lemon oil, see p. 31 of this *Report*.

Mandarin Oil. — The mandarin trees blossomed very profusely, but in the meantime a lot of the undeveloped fruit has fallen off. Yet the coming crop promises to be a very good one.

Already very high prices have been paid for the hanging fruit; meanwhile agreements for the delivery of the new oil have not been concluded.

In conclusion it must be pointed out the important rôle played by the variations of the rate of exchange abroad and on the markets here, in fixing the price of the essential oils of South Italy.

Italy has had a bad corn harvest, also a bad harvest of leguminous plants; hence it will be compelled to import greater quantities of corn than usual in order to feed its population.

Drought and heat have damaged the very promising wine and oil crops; the industries of Upper Italy are suffering severely under the repeatedly renewed trade disturbances; an unsatisfactory commercial position for Italy during the next year results from this, and thereby appears to be the prospect of a high rate of exchange for abroad.

High rates of exchange for abroad mean for inland Italy, increase in value of her own products, and hence probably comparatively high prices for essences.

Re trade in mandarin oil during last years, see p. 25 of this *Report*.

Re adulteration of mandarin oil, see p. 32 of this *Report*.

Orange Oil, sweet. — Under the influence of the extraordinarily high value of this oil which still prevailed in April, and in spite of the splendid blossoming of the trees, almost the whole of the coming crop was bought on the trees from the land owners in the early part of the year at foolishly high prices.

In the unhealthy, over-eager competition of the traders amongst themselves, 60 lire per 1000 oranges, and then more and more till 100 lire were paid.

Unsold gardens scarcely existed, for the land owners had never before experienced such prices. — The mentioning of this extraordinarily high price paid for the raw material is sufficient for one to come to the conclusion that the buyers of oranges, for whaterer purposes they may have purchased them, will be forced to price the fruit or its waste as dear as possible, unless they would lose whole fortunes by these deals.

This year's over-rich blooming of the orange trees has not yielded what it promised chiefly on account of the lack of water and the extraordinarily warm spring which have occasioned a considerable falling off of the young fruit. This is all in favour of the above mentioned buyers.

It is easy to see, in contemplating the high fruit prices and the tremendously elevated net costs, that the oil producers would like to see nothing better that a chance of mixing afresh in the local speculations in order to pull themselves out of the mess in which they find themselves through their dear purchases of fruit. The speculators on their side come upon a not altogether too difficult field for their activities to work upon.

Under these conditions, the local prospect of the development of the orange oil market of these districts depends more than ever before on the more or less favourable results of this year's orange harvest in Cuba, and the fixing of the price of the oil on that island.

Re production of orange oil in Italy during recent years, see p. 25 of this *Report*.

Re winning of orange oil in the West Indies, see p. 32 of this *Report*.

Re an adulterated sweet orange oil, see p. 31 of this *Report*.

Essence Export of the Year 1919.

According to the Report of the Italian Finance Ministry.

Destination	Bergamot Oil. Quantity		Value
France	kg.	93761	
Great Britain	„	39785	
Russia	„	110	
Sweden	„	1139	
Switzerland	„	5635	
U. S. A.	„	37833	
Other Countries	„	16257	
	Total: kg.	194520	Lire 14589000

Lemon Oil.			
France	kg.	103198	
Great Britain	„	221385	
Russia	„	317	
Switzerland	„	36129	
Australian Federation	„	23832	
The Argentine	„	6068	
U. S. A.	„	312077	
Other Countries	„	54733	
	Total: kg.	757739	Lire 12123824

Orange Oil.			
France	kg.	36270	
Great Britain	„	15664	
Russia	„	—	
Switzerland	„	5156	
U. S. A.	„	34593	
Other Countries	„	12230	
	Total: kg.	103913	Lire 4156520

Mandarin Oil.		Other Oils.	
kg. 4041	Lire 323280	kg. 2374	Lire 118700

Bergamot Oil. — According to a report of the American Trade Attaché[1]) in Rome, more bergamot oil was exported from Italy during the first five months of 1919 than during the years 1917 and 1918. Of this export, which amounted to 77088 kg. and was valued at £ 5781600, 38058 kg. (about 50 per cent.) went to France, 15432 kg. to U. S. A. and 14878 kg. to England.

It must sound somewhat peculiar to the reader, when he reads further on in the report that bergamot oil is won in Sicily[2]). Especially interesting is further the announcement of the Trade Attaché, that the roots! of the bergamot tree yield by

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[1]) *Commerce Reports. Daily Consular and Trade Reports*, issued daily by the Bureau of Foreign and Domestic Commerce, Department of Commerce. Washington No. 108, May 7, 1920. — [2]) As is well known, the bergamot tree is cultivated exclusively in Calabria, since it does not thrive in Sicily.

distillation the product known as bergamot oil. The Sicilian peasant may be at liberty to distil bergamot roots as he wishes; however, the product must be first sent to Messina and there inspected by the authorities. American agents bought up the whole harvest months before the distillation.

Re bergamot harvest during recent years, see pp. 23 and 27 of this *Report*.

Lemon Oil.—Already in our last *Report* in discussing an adulterated cassia oil, we had remarked that people were not so sparing in adding phthalic acid ester as formerly; for the original idea of the raising of the ester content very often does not come into question at all[1]). In this inglorious field a small Leipzig firm has especially distinguished itself, on account of which it has been mentioned many times in our last *Report* (pp. 15, 38, 63, 69); and also again this time many oils originating from them came to us for examination which were adulterated in the manner mentioned. Amongst them were a lemon oil and a sweet orange oil, which we will discuss together in order not to repeat ourselves. Each had experienced an addition of about 50 per cent. phthalic ester, an amount which naturally had a strong influence on the constants of oils. The determination of the specific gravity and the optical rotation alone sufficed to recognise the adulteration.

	Lemon Oil.		Orange Oil, sweet.	
	Sample	Limiting Values	Sample	Limiting Values
$d_{15°}$	0.9813	0.856 to 0.851	0.9622	0.848 to 0.853
$\alpha_{D20°}$	$+31°25'$	$+57°$ to $+61°$	$+34°20'$	$+95°30'$ to $+98°$

A saponification gave information as to the adulterant; whilst the ester value of lemon oil and orange oil is normally quite insignificant, in the above two cases it was abnormally high (262.6 and 237.1 respectively). According to this an ester had been used, which on further investigation proved to be phthalic acid ester. Judging by the constants both oils, as already mentioned, had been adulterated to the extent of about 50 per cent.

Re information about the adulteration of lemon oil, A. Guido[2]) has published a work. The determination of the specific gravity, and the rotatory power does not always suffice to prove adulteration in the case oils skilfully adulterated with terpenes, sesquiterpenes or citral. On the other hand in cases where it can be established that foreign substances have been added to the oil, one ought to test the solubility in alcohol of as many fractions of the sample as possible.

Guido prepared a mixture of 270 cc. of lemon oil, 30 cc. of limonene, 0.9 cc. of pure citral and 0.6 gm. sesquiterpene. By means of the usual constants ($d_{15°}$ 0.8600; $[\alpha]_D$ $+60°52'$, critical solubility temperature[3]) 66.1°) this artificial product was indistinguishable from the genuine oil. The boiling points also of 25 various fractions of each kind of both oils agreed very closely. On the contrary the critical solution temperatures of the corresponding fractions showed differences now and again; and amongst the last distillations there were remarkable differences which were conditioned by the varying content of both the samples in oxygenated ingredients.

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[1]) *Report* 1919, 15. Cf. also there pp. 14, 38, 63, 69. — [2]) *Sulle essenze di limone. Estr. Annali R. Stazione di Agricoltura e Frutticoltura* Vol. IV, p. 209. (The date of the year is missing in the Original.) According to kindly forwarded special reprint. — [3]) This manner of nomenclature of Guido's has nothing to do with a critical temperature in the scientific sense.

For estimation purposes 2 cc. of the fraction to be tested, and 2 cc. of 89 per cent. alcohol were placed in a suitable test-tube dipping into a water both which was gradually heated. The critical solution temperature was reached at the moment when the cloudy fluid became clear, and could be read from the thermometer dipping into it. This experiment is said to be very sensitive; but only painstaking and exact work, and above all the adherence to exactly similar experimental conditions, lead to success. The practical value of Guido's method can only be judged after further experiments. The adulterated tests with which we had to do, were on the whole less cleverly composed; and consequently the adulterations could be proved by the customary methods[1]).

Re production of lemon oil during recent years, see pp. 23 and 28 of this *Report*.

Mandarin Oil.—A mandarin oil forwarded to us from Sweden to pass an opinion on showed very grave variations from the norm, as is seen from the following comparison:—

	Sample	Limiting Values
$d_{15°}$	0.8494	0.854 to 0.859
α_D	$+93°\,2'$	$+65°$ to $+75°$
α_D of 1st 10 per cent. of distillate	$+92°\,32'$	slightly lower or up to 2° higher than α_D of the original oil
$n_{D20°}$	1.47279	1.475 to 1.478
Acid value	0.9	up to 1.7
Ester value	6.0	5 to 11
Residue after evaporation	1.2 per cent.	2.4 to 3.5 per cent.

The discrepancies are shown in the specific gravity, in the refraction, and in the residue after evaporation, all of which are too low: but above all in the far too high optical rotation, which alone suffices to shew that the oil is strongly adulterated. Apparently terpenes of orange oil had served for the purposes of adulteration, and indeed in such quantities that could well exceed 50 per cent.

Re trade in mandarin oil during recent years and the mandarin crop of 1920, see pp. 25 and 28 of this *Report*.

Orange Oil.—Since 1911, as we have already often reported[2]), this oil is obtained in large quantities from sweet oranges in the West Indies. We find more exact data over this continually flourishing industry in a paper by Hood[3]); here especially, a new machine is illustrated and described with which all kinds of agrumen fruits can be peeled. Up to now the orange oil has been obtained everywhere by the écuelle process[4]). Apart from the small yield of oil which this method produces, only the best fruits completely free from all spot or blemish are used, and a considerable quantity of rejected fruit remains. These oranges of less value are packed in so-called plain wrappers in the West Indies and are sold for immediate use in the neighbouring ports.

The new peeling process by means of machinery now permits the obtaining of the esssential oil, even from this second-class of oranges. With help of this machine, built by the United States Department of Agriculture and patented in that country, a workman can peel 2 tons of oranges or 3½ tons of grape fruit in an hour. In this process the oil cells are opened, and the peel leaves the machine in a finely divided condition, so

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[1]) Cf. *Report* April 1913, 60; *Report* 1918, 24; *Report* 1919, 26. — [2]) *Report* April 1915, 22; *Report* 1918, 24. — [3]) *Bulletin* 399, *U. S. Dept. of Agriculture*. — [4]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 2.

that it can at once be further worked up. The superfluous fruit, which is not put to any use in the écuelle process, is used for the preparation of marmalade or orange syrup.

The machine consists of the four following important parts:—

(1) A rapidly revolving, 11 ft. long drum, which scrapes the peel off the fruit.

(2) A connecting spiral spindle of the same length, which moves the fruit along the drum, and takes away the peelings.

(3) A specially constructed table, which serves as a support for the fruit whilst passing through the machine.

(4) A contrivance for adjusting the space between drum spindle and table to the size and shape of the fruit.

Experience in the use of the machine has shown that the peel removed by the first third of the length of the drum contains about 76 per cent. of the oil, that removed by the second third about 23 per cent. and the peel removed by the remaining third contains less than 1 per cent. of the oil. Hence only the peel removed by the first $^2/_3$ of the drum is used in the further manufacture; it is stirred up with a little water and is distilled in a special vacuum apparatus. The best results are obtained when the body of the still is heated externally simultaneously with the use of direct steam. The distilled oil is mixed with 20 per cent. of its weight of fresh unextracted peel, macerated and filtered. The oil has a lemon-yellow colour after this treatment, with a light brown shine, a very fine odour, and the characteristic aromatic taste of oranges.

As during maceration about 10 per cent. of the distilled oil is retained by the fresh peel, the filter residue is compressed into cakes, and subjected to steam distillation. In this way almost the whole of the oil in the peel can be obtained. In order to separate the expressed oil, obtained as a thick emulsion, from the water, it is heated to 90° in the water-bath and $^1/_{10}$ of its volume of a 10 per cent. gelatine solution is added, and a fourth of its volume of a 10 per cent. tannin solution. In this way the substances which bring about the emulsification are coagulated, and the essential oil can be obtained without loss by pressure. The rhizome of "saw palmetto" proved itself to be a cheap source of tannin, since it contains about 7.6 per cent. of tannin.

A comparison of the oil obtained by vacuum distillation, and that obtained by pressure with a hand-pressed oil from Italy showed that all samples had the same fine characteristic aromatic taste and smell. The machine-pressed oil excelled both other samples in its fine fruity aroma.

		Colour	Smell	$d_{25°}$	$[\alpha]_{D25°}$ [2])	Residue on evaporation
Italian oil		Lemon yellow [1])	Characteristic smell of oranges	0.8415	115° 6′	1.73 per cent.
Florida	Distilled oil .	Lemon yellow with a slight brown glint	ditto	0.8423	115° 18′	2.10 „ „
	Pressed oil .	Reddish yellow	Characteristic smell of oranges; fruit flavour	0.8445	109° 36′	2.90 „ „

Hood comes to the conclusion that a good marketable article is obtained by the vacuum process, and a thoroughly excellent oil by pressure. If the good yield and

[1]) Remarkably light for Italian oil; Italian oils mostly have a brownish tinge. — [2]) From this as original rotation would be reckoned: $\alpha_D + 96° 51'$, $\alpha_D + 97° 7'$ and $\alpha_D + 92° 33'$.

the utilisation of the raw material are reckoned together the method can be regarded according to Hood's views, as a great advance in the West Indian orange oil industry[1]).

Re production of orange oil in South Italy during recent years, see p. 25 and 29 of this *Report*.

Re an adulterated sweet orange oil, see p. 31 of this *Report*.

Eucalyptus Oil.—There was no shortage of good globulus oil since the end of the war; Spain especially delivered considerable quantities, which for very good reasons found its way chiefly to Germany. As we hear, the production in Spain has considerably increased, and can take up the competition with the Australian oil especially as regards quality. *Amygdalina* oil was only offered in very small quantities, and appears to fall short of the demand by far, as in pre-war days, when it was sought for vairous technical purposes.

At present there are about 200 eucalyptus oil factories in Australia, fifty of which are on Kangaroo Island, six in Adelaide, four in Tasmania and one in Queensland. Besides the oils used in medicine and in the smelting and metallurgical industries — *Eucalyptus Globulus*, Lab. and *Eucalyptus amygdalina*. Labill. and the corresponding varieties — oils of lesser used sorts are now prepared as that of *Eucalyptus Macarthuri*. Deane and Maiden and *E. citriodora*. Hook. for the production of geraniol, citronellol (citronellal?), geranyl acetate &c.[2]).

In Victoria 1917 to 1918 806977 lbs. of eucalyptus oil were distilled which exceeded the yield of the previous year by 161 tons. The "Blue mallee" (*Eucalyptus polybractea*, R. T. Baker) which grows in the territories of the north-west is now systematically cultivated. In the Wombat Forest, where many small distillation establishments are at work, only the "peppermint tree" (*E. piperita*, Sm.) is used. Several larger works are in Bendigo (Sandhurst), which use the leaves of "Red" and "White Ironbark" (*E. siderophloia*, Benth. and *E. paniculata*, Sm.). These shrub-like plants are still to be found in great quantities in the neighbourhood[3]).

The phosphoric acid method for the estimation of cineole, which from our experience and that of others most be classed as untrustworthy[4]), has again been thoroughly tested by C. T. Bennett and M. S. Salomon[5]). They come to the result, that the most accurate results are obtained with a eucalyptole content of under 85 per cent. if one proceeds exactly according to the British pharmacopœia and uses 5 cc. of phosphoric acid. Both the phosphoric acid and the arsenic acid process give low results with a high eucalyptole content. The method however suffices for the purposes of the pharmacopœia. These explanations do not alter the unfavourable opinion we have formed of the phosphoric acid process.

Eucalyptus oil produces apparent symptoms of poisoning if taken in large quantities[6]). According to P. Auerbach[7]) such a case happened to a workman. He was unconscious for half an hour after taking 20 cc. of eucalyptus oil; but he was again

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[1]) Cf. *Chemist and Druggist* **91** (1919), 878. — [2]) *Chemist and Druggist of Australia.* According to *Chemist and Druggist* **92** (1920), 746. — [3]) *Chemist and Druggist of Australia.* As per *Journ. Soc. Chem. Ind.* **39** (1920), R. 167. — [4]) Cf. *Report* October **1915**, 15. — [5]) *Perfum. Record* **10** (1919), 211. — [6]) Cf. *Report* October **1906**, 37; October **1911**, 49. — [7]) *D. Med. Wochenschrift* **45** (1919), 1165 as per *Pharm. Ztg.* **64** (1919), 846.

brought to by large doses of milk. A closer examination showed that the oil contained no dangerous impurities.

In another poisoning case, which occurred in Württemberg in 1918, the eucalyptus oil proved to be an artificial product composed of 6 per cent. alcohol, 30 per cent. camphor with some camphor-containing camphor oil fractions, and waste-terpenes[1]).

Re oil of *Eucalyptus megacarpa*. F. v. Müller, that up till the present had not been examined, H. G. Smith[2]) reports: — The oil contains pinene, limonene, dipentene, about 30 per cent. cineole and probably 10 per cent. terpinene, that was found in the fraction boiling between 170 to 190°. Terpinene was indicated by the nitrosite (m. p. 155°), and by rapid oxidation in the cold with Beckmann's chromic acid mixture. During this reaction the inactive terpinene was destroyed and the residue consisting chiefly of limonene increased in optical activity.

Fennel Oil. — During this year the prices of fennel oil have kept at their previous level, and the approach of the new harvest has only slightly influenced the market. The yield of the Lützen fennel district is described as normal, and up to within a few weeks ago appearances led one to believe that one would be in the position to buy more cheaply this year. Unfortunately certain elements have appeared in the last few weeks in the fennel districts only a few kilometers from Leipzig which offer no resistance to the exaggerated demands of the peasants and by agreeing to high prices, for which reason foreigners are said to be in the market, they obtain large quantities. This year only small amounts will be procured for the distillation of fennel oil, for with the present prices there can be no thought of a profit. It should be noticed however that the reaction has set in only within the last few weeks, and it remains to be seen if surprises in the form of lowering of prices set in; if it turns out not to be true that large quantities from the previous year turn up.

Geranium Oil. — It is announced that the supplies of African oil are meagre and also that the supplies from the last harvest are quite exhausted; consequently high prices must still further be reckoned with. Pure ordinary Algerian distillates finally reached 325 francs per kilo, against about 45 francs before the war. Quantities of Réunion geranium oil are still to be had; but a falling of the price, which hovers in the neighbourhood of 325 francs per kilo, is scarcely to be reckoned with.

Of three Japanese geranium oils examined by S. Furukawa[3]), that of *Pelargonium denticulatum*, Jacq. was similar in composition to the geranium oils of commerce, whilst the oils of *P. graveolens*, L'Hérit. and *P. Radicula*, L'Hérit. were of little value as perfumes. The chief ingredients of *P. graveolens*, *d*-citronellic acid 56 per cent.?, *l*-menthone, and *l*-citronellol were isolated. Moreover the following data *re* oils were supplied: —

	P. graveolens	*P. Radicula*	*P. denticulatum*
Density	0.9178	0.9234	0.8860
Acid value	183.68	5.6	7.17
Ester value	4.8	31.7	12.8
Total geraniol	23.1 per cent.	26.3 per cent.	63.5 per cent.
Free geraniol	22.0 per cent.	17.26 per cent.	60.0 per cent.
Yield from fresh plants	1.75 to 2 per cent.	1.5 per cent.	5 per cent.

[1]) *Südd. Apotheker-Ztg.* 59 (1919), 972 as per *Chem. Zentralbl.* **1920**, I. 539. — [2]) *Journ. and Proceed. Roy. Soc. N. S. W.* 52 (1918), 529, as per *Soc. Chem. Ind.* 39 (1920), A. 206. — [3]) *Journ. chem. Ind. Tokio* 22 (1919), 83. According to *Journ. Soc. chem. Industry* 38 (1919), A. 656.

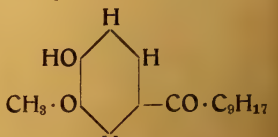
The oil obtained from *P. graveolens* had according to Furukawa quite different characteristics from the oils of *P. graveolens*, L'Hérit. from the East Indies (Nilgiri Hills)[1]) and of *P. graveolens*, Ait. (*P. terebinthinaceum*, Cav.) from Algiers[2]). Over 70 per cent. total geraniol was found amongst other things in the two last-mentioned oils; and it is to be assumed that the species described by Furukawa as *P. graveolens* is identical with either *P. graveolens*, L'Hérit. or with *P. graveolens*, Ait.

That a verification of the constants alone is not always sufficient, was shown in the examination of a sample of African geranium oil. The oil offered us for sale had the following properties: — $d_{15°}$ 0,8992, α_D — 7° 10′, $n_{D20°}$ 1.47053, acid value 5.4, ester value 51.8 = 21.8 per cent. geranyl tiglinate, ester value after acetylation 226.8 = 75.1 per cent. total geraniol, soluble in 1.5 volumes and more of 70 per cent. alcohol. Accordingly the sample should be reckoned as normal, especially as the odour was satisfactory. But a more searching examination of the last-mentioned property by comparison with an oil guaranteed pure, raised certain doubts, which were finally proved to be well founded. It turned out that the oil contained ingredients which reacted with sodium bisulphite, which does not happen in the case of a pure geranium oil. The bisulphite compound obtained was sucked off, purified and decomposed; when the odour of citronellal appeared. Unfortunately we only had a small amount of oil at our disposal, so that we were unable to further confirm the citronellal by forming a derivative, but we had to be satisfied with the evidence furnished by the smell. In any case it had been proved that something had been added to the geranium oil, and we are strongly of the opinion that it was a case of a geraniol obtained from citronella oil and adulterated with citronellal.

Less care was shown in a similarly adulterated African geranium oil. In this case a distinct odour of citronella oil was noticeable, in addition the optical rotation and ester value were too low: — $d_{15°}$ 0.8963, α_D — 3° 4′, $n_{D20°}$ 1.47191, acid value 1.8, ester value 21.0 = 8.9 per cent. geranyl tiglinate, ester value after acetylation 221.2 = 72.9 per cent. total geraniol, soluble in 1.5 volumes and more of 70 per cent. alcohol, diluted solution cloudy. This oil reacted more vigorously with bisulphite than the former; in splitting up the bisulphite compound with sodium carbonate citronellal was also obtained in this case. Judging by the smell, either citronella oil or at best a citronella oil fraction had served as adulterant.

Glycerin acetate was found to be another adulterant of geranium oil. There was only a small amount present in the oil in question; it was separated by shaking up with water many times; the aqueous extract was evaporated, leaving a 1.5 per cent. residue, which by its high saponification number, 506.2, revealed itself as glycerin acetate. Still, we have made mention of this observation here, for it shows in what a variety of ways the adulteration can be effected.

Ginger Oil. — H. Nomura has continued his investigations of the pungent substance in the ginger root[3]) and reports that the contained compound in addition to zingerone is Shogaol $C_{17}H_{24}O_3$, an unsaturated α,β-ketone with the following constitutional formula[4]): —



[1]) Cf. *Report* **1918**, 28. — [2]) Cf. *Report* Oct. **1913**, 62. — [3]) Cf. *Report* **1919**, 31. — [4]) According to *Journ. Soc. chem. Industry* **38** (1919), R. 309.

Lavender Oil. — This important oil also remains continually at a high figure, to which the consumers have not yet been able to accustom themselves. The hopes cherished shortly before the commencement of the new harvests, that the prices of 200 to 225 francs per kilo would sink have unfortunately been shattered by the results of this year's distillations. In consequence of greater dryness the work started a few weeks earlier than usual, and although a favourable result was predicted, extraordinarily high prices were asked for the flowers by the collectors. Only at the commencement was one satisfied with 45 francs, then prices were raised to 100 francs and here and there even to 120 francs per kilos. For these reasons it is clear that the prices of lavender oil with a high ester content, were fixed at a correspondingly high figure; and it is not surprising when as much as 300 francs per kilo were demanded for such qualities. No change in the position intervened in the markets at Digne, Sault and Apt, so that the turnover was small. The distillers are said to have made much money during the past year and are therefore not obliged to dispose of their products as quickly as possible. According to the opinion of our adviser, the further course of the prices depends most of all on the position which U. S. A. will adopt towards the new prices, when the European consumers still persevere in their natural policy of holding back. We learn however that very little desire to satisfy the demands is detected over there, since it has become known that an organisation of lavender oil distillers by means of wall placards in Grasse have published their resolution not to sell under 310 francs per kilo, since the harvest has been poor, the prices of blossoms very high, and the yield of oil very bad. An American firm[1]) has taken objection to this resolution in a circular directed to the American perfumers, in which it states that at the rate of exchange prevailing, the price for the consumer works out at $ 12.35 per lb.; although it has been proved that the harvest is an average one, and that considerable supplies from the previous year are still at disposal. It will be very interesting to learn, what position other consumers in the United States will take up with regard to the matter.

Two lavender oils originating from a factory at Grasse, which were offered to us for sale *via* Switzerland, show us that in Southern France firms even of good repute have recently betaken themselves to the slippery territory of adulteration, for neither of the two oils was pure. With the one marked "Fleurs" no special pains had been taken in the adulteration, some phthalic ester having been merely added. This made the specific gravity too high ($d_{15°}$ 0.8974), so that the adulteration was very quickly noticed. The adulteration of the second sample — "Quintessence douce" — had been effected much more skilfully, for here was, apart from the insufficient solubility, which however might depend on the method of obtaining the oil, there was nothing noticeable to remark *re* the usual constants; and suspicion was first awakened when determining the acid value II. The estimation proceeded in the well-known way[2]) that the acid value and ester value were first found as usual, then the content of the saponification flask was evaporated to dryness, and then the residue acidified with sulphuric acid was subjected to steam distillation. With pure lavender oil almost the whole of the acid present passes over with the steam; and the quantity can be determined by titration. The acid value II thus obtained is in the case of lavender oil only slightly lower than the saponification value (acid value + ester value); up to the present in

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[1]) *Drug. and Chem. Markets* VII, No. 12, p. 615. — [2]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III p. 72.

the case of pure oils we have found a difference of 5 at the highest[1]), and if it even happened to be a trifle higher, it was always a result of resination, and it at once sank when the oil had been rectified. Otherwise with oils adulterated with esters of acids not volatile in steam (succinic acid, phthalic acid and the like). The too high difference remains here also after the rectification of the oil.

With the above mentioned "Quintessence douce" this difference amounted to nearly 12, and besides during the distillation a flocculent substance separated out in the receiver, which otherwise is never the case. It was also remarkable, that the acid did not pass over so rapidly and easily as under normal conditions, so that the end point of the distillation was only reached with difficulty and the acid value II was consequently not to be estimated sharply.

In order to obtain information as to the nature of the flocks, they were collected on a filter and dried. In the course of further testing it was found to be an acid, which melted at about 31° and had an acid value of about 236. Since we only had a trace of the substance, and the small oil sample for the examination was used up, a purification of the acid was out of the question and we had to rest satisfied with this approximate verification. The numbers do not agree with any one of the known fatty acids, yet we shall hardly go wrong in the assumption that we had been dealing with a somewhat impure lauric acid (melting point 43.6°, acid value 279.7). Since this does not form one of the components of lavender oil, it can only be regarded as an adulterant, which had been doubtlessly added in the form of ester, for the oil contained practically no free acid. It cannot be said how much ester had been added, since it was impossible to estimate the acid that had passed over apart from the others, and also since the acid had apparently not been completely distilled over. Yet however the observant analyst is at least in the position in general to recognize the adulteration. The admixture is all the more remarkable, since the oil, as already mentioned, showed normal constants and was comparatively poor in esters:— $d_{15°}$ 0.8889, α_D — 9°20′, acid value 0.9, ester value 72.3 = 25.3 per cent. ester, reckoned as linalyl acetate. It is seen from this how necessary it is to carry through the investigation in all its details, if one wishes to be accurately informed of the purity or otherwise of an oil.

We have been able to establish the same adulteration in two further lavender oils which had been forwarded to us by various parties to pass an opinion on. We have no doubt that they originally come from the same French source as the sample we have just discussed; the one oil (II) indeed appears to have passed through one or more stages, for it was adulterated almost beyond recognition. Here are the constants:—

	I	II
$d_{15°}$	0.8892	1.0275 (normal 0.882 to 0.896)
α_D	— 5°11′	— 2°18′
Solubility in 70 per cent. alcohol	soluble in 3.3 vols. and more, diluted solution opal	1.5 vols. and more
Acid value	0.5	0
Ester value	99.7	248.3
Acid value II	about 88.0	about 80
Difference between saponification value and acid value	about 12.2	about 168.3

Here also, in both cases, in estimating acid value II the same flocculent substance separated out in the receiver, as was the case with the afore-mentioned sample,

[1]) In an earlier *Report* (October 1912, 76) we gave 3 as greatest difference, this is however according to our experience in the course of the years rather too low.

and further we were enabled to observe this time also, that acid value II did not allow itself to be sharply estimated. Unfortunately only very small samples were at our disposal, and again it was impossible to exactly identify the acid in question.

Whilst with oil I one had been satisfied in adding one adulterant, and had done it with so much foresight that it was only recognizable on closer examination, it was too high specific gravity, and then by the quite impossible ester value, which would just the contrary for oil II. Here the adulteration was at once betrayed by the far correspond to a content of 86.9 per cent. of linalyl acetate. The oil had been manipulated, as was shown in the course of further analysis, in a manner quite unheard of, for besides the conjectured ester of lauric acid, glycerin acetate and the ester of phthalic acid were proved to be present.

The last-named adulterant occurred in a further lavender oil that we also had to pass an opinion on. This was not the only adulterant present but it amounted to about 50 per cent. This was naturally shown strongly in the specific gravity and in the ester value:— d_{150} 1.0226, acid value 0.9, ester value 323.2. This last would correspond to a content of linalyl acetate of 113 per cent., whilst in reality only 14 per cent. was present, as was seen from acid value II (39.2).

Lime Oil.—After the conclusion of the War further advances in the lime industry are to be noted in the Leeward Islands and in British Guiana, on the satisfactory development of which we have already reported[1]). Not only on Dominica, St. Lucia and Trinidad, but also on Antigua, Nevis and Tobago successful efforts are being made, to improve the processes for winning the oil, and to protect the lime plantations against diseases and insect damage by careful culture. Hence the plant raisers were requested to spray the young lime trees regularly on account of insects, to protect then with wind screens, and if necessary to drain the land. The Government Lime Factory at Onderneeming (British Guiana) yielded in the period from April 1st 1917 to March 31th 1918 a net profit of 16 per cent. on the invested capital[2]).

Linaloe Oil.—Various large lots of Mexican oil have arrived, but on account of the low value of the mark, the prices keep about the same as last year.

The imports of Cayenne oil *(Bois de rose femelle)* were very small, and only recently have the offers increased, but still at unchanged high prices.

The amounts exported from French Guiana are as follows[3]):—

1890 to 1899	1384 kilos	1914 . . .	39569 kilos
1900 „ 1909	5369 „	1915 . . .	24668 „
1910 . . .	22147 „	1916 . . .	33119 „
1911 . . .	42642 „	1917 . . .	31044 „
1912 . . .	35936 „	1918 . . .	19276 „
1913 . . .	44676 „	1919 . . .	13913 „

From these figures the significant set-back in the production is noticeable.

Oil of a Mentha species.—F. Elze[4]) gives some data *re* the essential oil of a *Mentha* species growing in large quantities in the stubble-fields of Central and Northern France, which is probably a hybrid of *Mentha piperita*, L. and *M. Pulegium*, L. By steam

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[1]) Cf. *Report* **1919**, 34. — [2]) *Perfum. Record* **10** (1919), 187. — [3]) *Chemist and Druggist* **93** (1920), 944. — [4]) *Chem. Ztg.* **43** (1919), 740.

distillation 0.1 per cent. of oil was obtained containing 40 per cent. total alcohol, a little menthol and rather a large amount of pulegone, it possessed the following properties:— $d_{15°}$ 0.920, $\alpha + 8°$.

Oil of Monarda fistulosa.—Further details about the identification by Miller[1]) of the constituents found in the oil of *Monarda fistulosa*, L. now lie before us, which are here reproduced[2]):—

α-Pinene, which is present as a mixture of the dextro- and lævo-varieties, was identified by the nitroso chloride (melting point 103°), the nitrolbenzylamine (melting point 123 to 124°) and the nitrol piperidide (melting point 117 to 118°). The presence of di-hydro cumine alcohol was given by the obtaining of a semicarbazone (melting point 198 to 199°) and the high boiling point (225 to 245°) of the free oil. Butyraldehyde and *iso*valeraldehyde were identified by the *p*-nitrophenylhydrazones of melting points 90 to 92° and 111° respectively, and acetic, butyric, valeric, and caproic acids were identified by means of their silver salts.

Oil of Mosla grosserrata.—*Mosla grosserrata*, Maxim. is a wild-growing annual labiata known by the name of *Himeshiso* in Japan, with oval leaves, and purple-coloured blooms in clusters, which become from one to two feet high. On distilling the fresh weed which had ceased to bloom, S. Furukawa obtained an essential oil with the following properties:— $d_{15°}$ 0.9137, $[\alpha]_D$ — 3°, acid value 0. The oil contained 25 per cent. carvacrol, 1 per cent. thymohydroquinone, 0.5 per cent. thymoquinone and thymoquinhydrone. About 40 per cent. cymene was isolated from the phenol-free oil (d 0.8841; ester value 17.68; ester value after acetylation 51.2). Phellandrene and terpinene were also identified. How the individual constituents were identified is not mentioned in the report[3]).

Oil of Mosla japonica.—Various authors formerly gave conflicting details *re* the chief constituents of the oil of the labiata *Mosla japonica*, Maxim. *(Yamashiso)*[4]). An explanation of this is given by K. Hoshino[5]) who has established that either thymol or carvacrol, but never both constituents together are found in the same oil[6]). An oil containing thymol had the following properties:— d 0.9154, α_D 1.0° (direction of angle of rotation not given), $n_{D20°}$ 1.4996, ester value 4.5, thymol content 50.06 per cent. It was almost insoluble in 70 per cent. alcohol, but dissolved in 2 vols. 80 per cent. alcohol. For estimation of the terpenes, the phenol-free oil was distilled over sodium, and collected in six fractions. The presence of phellandrene, p-cymene, γ-terpinene, caryophyllene, cadinene, and probably sabinene were established. More exact information is wanting in the report.

Oil of Mosla punctata.—The air-dried weed of the labiata *Mosla punctata*, Maxim. contains according to Y. Murayama[7]) about 1 per cent. of a yellow, pleasant smelling essential oil with the following constants:— $d_{4°}^{16°}$ 0.8966; α_D — 9.06°; ester value 16, ester value after acetylation 36.4. As chief constituent the ketone "α-mujone"[8])

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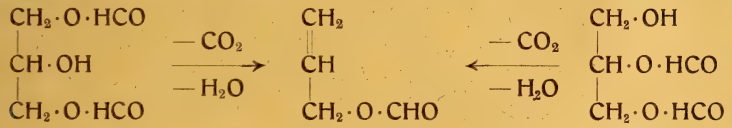
[1]) Cf. *Report* **1919**, 35. — [2]) Circular 4, Univ. of Wisconsin, October **1918**. — [3]) *Journ. chem. Ind. Tokyo* **22** (1919), 382. According to *Journ. Soc. chem. Industry* **38** (1919), A. 877. — [4]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 561. — [5]) *Journ. chem. Ind. Tokyo* **22** (1919), 557. According to *Journ. Soc. chem. Ind.* **38** (1919) A. 877. — [6]) Apparently the same phenomenon came to light here, as we observed with *Thymus vulgaris*, L. In thyme also, there is occasionally found in place of the usual thymol, its isomeride carvacrol. — [7]) *Yakugakugasshi*, **1919**, 450, 663. According to *Perfum. Record* **11** (1920), 11. — [8]) Perhaps α-thujone is meant.

was identified. The high-boiling-point fractions contained a sesquiterpene $C_{15}H_{24}$ (b. p. 125—128° at 12 mm. pressure); $d_{4^\circ}^{16^\circ}$ 0.9259; α_{D16° +2.16°; n_{D16° 1.5162. Phenolic constituents were not contained in this oil as in the oils of other *Mosla* species.

Mustard Oil. — In examining various kinds of mustard seed A. Cauda[1]) found that those of the black mustard *Brassica nigra*, Koch, contained more volatile mustard oil than those of *Brassica carinata*, A. Braun, and *Sinapis alba*, L. Also the amount of volatile oil is said to be greatest in plants from the northern districts and in plants with small seeds.

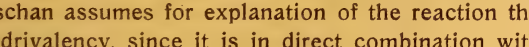
This work generally confirms the results of earlier investigations[2]). But it should be mentioned that a higher amount (1.07 to 1.17 per cent.) of volatile oil was found[3]) also in seeds of black mustard from southern countries, as East India (Bombay) and Greece.

O. Aschan[4]) published a paper on allyl compounds. These substances occupy a special position amongst the other groups of the fatty series in so far as they contain the ethylene radicle in direct combination with the simply substituted methyl radicle. The vinyl radicle stipulates the additive property, and the other characteristic transformations of the ethylene bodies, lessens however the bond of the methylene group for negative atoms and radicles, which consequently can only bind weakly the aldehyde group. Aschan succeeded in obtaining the diformylester (α- and β-form) of glycerin, by heating together glycerin and 93 to 95 per cent. formic acid, which easily changed into allyl formate by splitting off water and CO_2 at 190 to 260°. Allyl formate is a suitable and cheap raw material for the preparation of allylalcohol and other allyl compounds. The process which produces 60 to 70 per cent. of the theoretical yield of allyl formate, and permits of the recovery of large quantities of 30 to 50 per cent. formic acid by distillation, is suitable for the production of the ester on a large scale.



α-Diformin. Allyl formate. β-Diformin.

Allyl formate is a very reactive compound on account of the ethylene and carbonyl bonds in the molecule. Thus with concentrated caustic soda solution or milk of lime in a pasty condition up to 85 per cent. of allyl alcohol is obtained from the ester. Allyl chloride can also be obtained by passing HCl into the boiling ester in the presence of zinc chloride. Thus a new reaction for the formation of aliphatic halogen compounds is found. Aschan assumes for explanation of the reaction that the ester oxygen easily assumes quadrivalency, since it is in direct combination with the allyl group, and the likewise unsaturated keto group in the formic acid residue; then a splitting up into formic acid and allyl halogen takes place.



By the action of water-free oxalic acid on allyl formate, acid allyl oxalate was formed and small quantities of the neutral diallyl oxalate as by-product. Upon the

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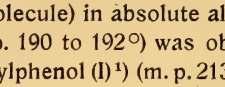
[1]) *Staz. sperim. agrar. ital.* **52** (1919), 122. As per *Chem. Zentralbl.* **1919**, III. 342. — [2]) Cf. *Report* Oct. **1915**, 29. — [3]) Cf. *Report* **1916**, 38. — [4]) *Oefversigt af Finska Vetenskaps-Societetens Förhandlingar* **61** (1918/19). Afd. A. Nr. 8.

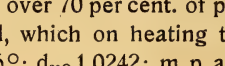
peculiar chemical nature of the allyl radicle — the analogous preparation of ethyl or benzyl mustard oil did not succeed — rests the formation of allyl mustard oil from allyl oxalate and potassium thiocyanate. Allyl thiocyanate is first formed, which an boiling the solution, changes into allyl mustard oil.

$$C_3H_5\cdot O\cdot CO\cdot COOH + K\cdot S\cdot CN = \underset{\text{Allyl thiocyanate.}}{C_3H_5\cdot S\cdot CN} + COOH\cdot COOK \longrightarrow \underset{\text{Allyl } \textit{iso}\text{thiocyanate.}}{C_3H_5\cdot N:C:S}$$

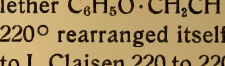
From allyl chloride (1 molecule), a solution of phenol (3 molecules) and sodium (1 molecule) in absolute alcohol, over 70 per cent. of phenolallylether $C_6H_5O\cdot CH_2CH:CH_2$ (m. p. 190 to 192°) was obtained, which on heating to 200 to 220° rearranged itself into *o*-allylphenol (I)[1]) (m. p. 213 to 226°; $d_{20°}$ 1.0242; m. p. according to L. Claisen 220 to 220.5°).



(I) *o*-Allylphenol.



o-Allylphenylmethylether.



o-Propenylphenylmethylether.

The methylether of the *o*-allylphenol heated to 125° with alcoholic potash changed into *o*-propenylphenylmethylether (m. p. 219 to 221°; $d_{20°}$ 0.9890), an isomeride of anethole. Its constitution was established by oxidising to salicylic acid methylether (b. p. 98 to 99°).

With ethylallylether (b. p. 64.5 to 66°; $d_{20°}$ 0.7618) a migration of the allyl group into the ethyl group on warming was not demonstrable.

Mustard oil is frequently used as a skin irritant in a 3 per cent. oil solution. Stronger effects can be obtained if the oil is used as an emulsion in sugar syrup, gum mucilage or a 3 per cent. tragacanth mucilage. According to G. E. Ewe[2]) the last-named proved to be especially suitable. The oil can be emulsified with the mucilage with the aid of a copper foam-beater. Comparative tests showed that a 2 per cent. oil emulsion in tragacanth mucilage has the same effect on the skin as a 3 per cent. mustard oil solution in a mixture of paraffin (15 per cent.) and yellow petrolatum (85 per cent.). The mustard oil tragacanth emulsion keeps very well, if kept in air-tight vessels — tin tubes for example.

Re estimation of essential oil in mustard seed, see p. 92 of this *Report*.

Orange Blossom Oil. — The well-known "Société coopérative des propriétaires d'orangers" have themselves manufactured into orange-blossom oil this year the huge quantities of flowers delivered to it by its members; unfortunately it results from this that the price of the pure distillate — about 2000 francs per kilo at beginning of harvest — reached 9500 francs by the end of May. There remained nothing further for the Grasse firms to do in order to obtain material for distillation but to pay high prices; and so it came about that the average price of the blossoms for the 1920 season amounted to 10 francs to 12 francs per kilo, although the harvest was a satisfactory one.

It is quite evident that only few consumers can invest in orange blossom oil at 9500 francs. Indeed the greater part of the oil still obtainable in the market consists moreover of "well decorated" goods, which can sustain no comparison with our artificial orange blossom oil (neroli), which, as a consequence, is in very great demand this year.

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[1]) Cf. *Reports* April **1913**, 144; April **1914**, 144; **1919**, 165. — [2]) *Americ. Journ. Pharm.* **92** (1920), 234.

Parsnip Root Oil. — By making a decoction of the dried roots of *Pastinaca sativa*. L.[1]). H. W. van Urk obtained an oil[2]) of a pleasant penetrating smell, and possessing the following properties: — $d_{40}^{17°}$ 1.077; α_D — 0° 39′; $n_{15°}$ 1.5328. It contained small quantities of vanillin, neither nitrogen nor sulphur, also acids and phenols not in noticeable quantities: — A few weakly doubly-refractive needle-shaped crystals were obtained from the oil.

Peppermint Oil, American. — The prices for American peppermint oil are still so high that they cannot enter into competition with the finest qualities prepared chiefly from Japanese oil which rule the European market, and hence for the time being the demand of our New York friends for the brands so beloved before the War, has entirely ceased. The last quotation was $ 6 per lb. for pure crude oil. The result of this year's distillation is described as normal.

As is known, the American Pharmacopœia, 9th edition, requires an ester content (menthyl acetate) of at least 5 per cent., and a total menthol content of at least 50 per cent.[3]). Already from the work published by Rabak[4]) in Bulletin 454 it goes forth that the menthol content as a matter of fact, increases with the growth of the plant, and that in most cases it amounted to less than 50 per cent.

This discovery was confirmed in the exhaustive investigations carried out by Fritzsche Bros., Inc., New York, with peppermint oil from Michigan. They examined all lots received by them in 1916, and collected the results in several tables, the average value of which is here announced: —

	Peppermint Oil.	Total Menthol.	Esters.
Entering from 14. VIII. to 30. IX. 1916	27130 lbs.	19911 lbs. = 47.59 per cent.	821.4 lbs. = 6.33 per cent.
„ „ 3. X. „ 13. XI. 1916	18946 „	9388 „ = 49.55 „ „	1191.7 „ = 7.02 „ „
„ „ 18. XI. „ 21. XII. 1916	18087 „	9286 „ = 51.34 „ „	1362.3 „ = 7.53 „ „
Total Quantities:	64163 lbs.	31585 lbs. = 49.23 per cent.	4409 lbs. = 6.87 per cent.

According to the above table, only the oil obtained in the late season satisfies the demands of the American Pharmacopœia with regard to the menthol content. On the other hand the ester content exceeds the lowest limit in all cases, and also otherwise the oils were of a very fine taste, and conformed to the pharmacopœia.

The low menthol content of the peppermint oil, which first became noticeable after the beginning of the War, must be chiefly ascribed to the circumstance that the planters, in consequence of the shortage of potash salts, could no longer manure their fields as formerly. Nevertheless, the deficiency of menthol diminished in no way the quality and fine taste of the oil, which in most cases is the decisive factor in passing judgement on it, and it were desirable that allowance were made for this fact in the American Pharmacopœia.

Peppermint Oil, Chinese. — Only a few investigations are available *re* Chinese peppermint oil obtained near Hong Kong probably from *Mentha canadensis* var. *glabrata*. Gray[5]). Y. Shinosaki has recently published the following information[6]). Chinese peppermint oil has a bright brown colour, a rather unpleasant odour, a bitter taste, and the following constants: — $d_{25°}$ 0.9091, $[\alpha]$ — 35° (in chloroform), $n_{25°}$ 1.4627, saponification value 29, ester value after acetylation 233, ester menthol 8.08 per cent., free menthol 70.75 per cent.; ketone (as menthone) 12.88 per cent.

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, page 378. — [2]) *Pharm. Weekblad* **1919**, 1390. According to *Heil- und Gewürzpflanzen* **3** (1920), 196. — [3]) Cf. *Report* **1918**, 57. — [4]) Cf. *Report* **1917**, 36. — [5]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 549. — [6]) *Journ. chem. Ind.* Tokyo **22** (1919), 458. According to *Journ. Soc. chem. Industry* **38** (1919), A. 877.

Peppermint Oil, Japanese. — After the Japanese producers and speculators have tried at various times during the summer to create a rise in the market on account of the dear lots of peppermint oil they have on their hands, a slackness has recently appeared, although a downward movement of the prices can not yet be spoken of. The conditions for such a movement were indeed there, for, apart from the trade slackness that had appeared, the unsold stocks from former harvests amounted in Japan at the end of August to about 4000 cases of menthol and 6000 cases of oil. Meanwhile estimations of this year's harvest are at hand, which state that the district of Bingo-Bitchiu can deliver about 150000 kin, and Hokkaido 250000 kin in a total of about 400000 kin. Under these conditions the keeping up of the price can only be described as artificial, and caused most of all by the bankers who made great advances on the dear stocks, and are now making every exertion to extricate themselves from this advancing business without loss.

For the German consumer, the fixing of the prices in the peppermint oil and menthol market is most of all a currency question, for even if a decrease in the values comes about shortly, it may be nullified by the fall in the value of the mark at the very least; a disparity may therefore enter between the sinking movement of the market and the falling in value of our currency.

Menthol. — According to a report of the *Oil, Paint and Drug Reporter*[1]) the Japanese menthol harvest of 1919 was estimated at 260000 lbs. of raw oil, which after distillation yielded about 2000 cases of 60 lbs. each, *i. e.*, 120000 lbs. menthol. According to the reports of the American consular agent in Tokio 400000 lbs. menthol were obtained in Japan in 1918, and 160000 lbs. in 1919.

The great lowering of the menthol production is due to the fact that the Japanese farmers are forsaking the cultivation of peppermint in favour of the wheat cultivation. The export of menthol during the last six years amounted to: —

1913	1914	1915	1916	1917	1918
306240 lbs.	355080 lbs.	429000 lbs.	509520 lbs.	331320 lbs.	312840 lbs.

During the same years America imported: —

940896 lbs.?	27962 lbs.	11020 lbs.	145203 lbs.	172776 lbs.	172450 lbs.

It is estimated that Japan uses on an average 75000 lbs. and Continental Europe 426000 lbs. menthol yearly.

We take the following data from another statistic[2]): —

	1909	1913	1917
Menthol production in Japan	147921 lbs.	258060 lbs.	561843 lbs.

A third announcement from Japanese sources per *Oil, Paint and Drug Reporter*[3]) states that the supplies in the various production districts during the season 1918-1919 amounted to 160000 lbs. in Yokohama and 441500 lbs. in Kobe, *i. e.*, a total of 601500 lbs.; the actual joint yield of the harvest in the Sambi and Hokkaido districts was 253500 lbs. Hence the disposable stocks for 1919/20 amount to 855000 lbs. By reason of the amounts which have been exported on an average since 1912, 726000 lbs. should be destined for export, *i. e.*, 330000 lbs. menthol crystals and 396000 lbs. oil.

From a publication of Raspe & Co., Kobe, *re* the characteristics of various peppermint oils, which contains chiefly the work of Y. Shinosaki (published in the *Kogyo-Kwagaku-Zasshi*) during 1915 and 1916 and has only just lately come into our possession, we select the following data: —

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[1]) *Ind. u. Handelsztg.* **1920**, 312. — [2]) *Chemist and Druggist* **92** (1920), 87. — [3]) *Ind. u. Handelsztg.* **1920**, 450.

The following quantities of menthol were obtained in the most production districts of Japan:—

	1912	1913	1914
Hokkaido	330000 kin	530000 kin	480000 kin
Sambi	150000 „	350000 „	130000 „
Yamagata	6000 „	5000 „	—

Stearoptene (menthol) and oil were exported from Japan in the following quantities:—

	Stearoptene		Oil	
	Weight	Value	Weight	Value
1912 . . .	133170 kin	1589729 yen	184885 kin	699250 yen
1913 . . .	232912 „	2872854 „	282115 „	1017678 „
1914 . . .	269266 „	1816096 „	277677 „	808809 „

The amount, which the Kitami branch of the Agricultural Experimental Station in Hokkaido obtained with foreign peppermint varieties in 1912, can be seen from the following compilation:—

	Dried drug per tan (= 1/4 acre)	Oil obtained therefrom	
		Weight	Per cent.
Herb of English origin . .	12250 momme[1])	126.0 momme	1.03 per cent.
„ „ German „ . .	7630 „	63.5 „	0.83 „ „

The yield in dried drug of the English variety has greatly diminished in comparison with former times. The reason may perhaps be ascribed to weather conditions and insect damage. The oil yield from the drug of German origin according to the percentage content has improved; the oils were weak brown and possessed the following constants:—

	$d_{25°}$	α_D	$n_{D20°}$	Solubility in 70 p. c. alcoh.	Combined menthol	Free menthol	Total menthol
Oil, English variety	0.9114	$\pm 0°$	1.4666	insoluble	5.22 p. c.	56.65 p. c.	61.87 p. c.
„ German „	0.9029	$-24.75°$	1.4647	„	2.57 „	63.09 „	65.66 „

The oils are distinguished from the Japanese oil by their higher refractive index, by their insolubility in 70 per cent. alcohol and by their smaller menthol content.

The oil of the Akamaru variety cultivated in Kitami was weak brown, but excelled the ordinary Hokkaido oil in taste and pleasant odour, and had the constants:— $d_{25°}$ 0.8946, α_D — 38° 31′, $n_{D20°}$ 1.4605, soluble in 2.8 vols. 70 per cent. alcohol, combined menthol 2.04 per cent., free menthol 74.47 per cent., total menthol 76.51 per cent.

The product distilled from fallen leaves had the constants:— $d_{25°}$ 0.9030, α_D —, $n_{D20°}$ 1.4613, soluble in 2.9 vols. 70 per cent. alcohol, combined menthol 5.42 per cent., free menthol 78.32 per cent., total menthol 84.74 per cent.

Japanese peppermint oil of the year 1912. — Oil samples were bought from manufacturers and export dealers. The samples obtained by the former had the following constants:—

	$d_{25°}$	α_D	$n_{D20°}$	Solubility in 70 p. c. alcoh.	Combined menthol	Free menthol	Total menthol
Hokkaido oil No. 1	0.8964	$-36.00°$	1.4597	2.7 vols.	1.58 p. c.	74.93 p. c.	76.51 p. c.
„ „ „ 2	0.8946	$-35.05°$	1.4597	2.7 „	2.57 „	69.52 „	72.09 „
Okayama oil No. 1	0.8976	$-39.50°$	1.4598	2.7 „	2.30 „	84.73 „	87.03 „
„ „ „ 2	0.8976	$-39.30°$	1.4598	2.8 „	1.32 „	85.71 „	87.03 „
„ „ „ 3	0.8954	$-38.63°$	1.4595	2.8 „	3.09 „	80.48 „	83.57 „

[1]) 1 momme = 3.7565 grammes.

In taste and smell the Hokkaido oil is the better, it is of a brighter colour than the Okayama oil. The Sambi oil has a more bitter taste than the Hokkaido oil.

The oil samples purchased by the traders turned out as follows:—

	$d_{25°}$	α_D	$n_{D20°}$	Solubility in 70 p. c. alcoh.	Combined menthol	Free menthol	Total menthol
Hokkaido oil No. 1	0.8951	—36.09°	1.4597	2.8 vols.	2.30 p. c.	68.02 p. c.	70.32 p. c.
„ „ „ 2	0.8975	—35.10°	1.4605	insol.	5.07 „	71.82 „	76.89 „
Sambi oil No. 1	0.8965	—35.77°	1.4598	2.8 vols.	4.17 „	70.83 „	75.00 „
„ „ „ 2	0.8963	—39.50°	1.4595	2.8 „	1.78 „	83.76 „	85.54 „

Hokkaido oil No. 2 was adulterated with 5 per cent. of a fatty oil. The Sambi oil contained as a rule 75 per cent. free menthol; the above figure (70.83 per cent.) is very low.

The constants of *Japanese peppermint oil for the year 1913* were as follows:—

	$d_{25°}$	α_D	$n_{D20°}$	Solubility in 70 p. c. alcoh.	Combined menthol	Free menthol	Total menthol
5 various oils from Okayama	0.8969 to 0.8976	—38.25° to —39.25°	1.4591 to 1.4597	2.6 vols. to 3.4 vols.	2.09 p. c. to 5.72 p. c.	79.47 p. c. to 84.71 p. c.	83.65 p. c. to 87.28 p. c.
9 various oils from Hiroshima	0.8955 to 0.9014	—36.25° to —40.38°	1.4589 to 1.4603	2.7 vols. to 3.4 vols.	1.83 p. c. to 6.57 p. c.	76.07 p. c. to 90.65 p. c.	81.32 p. c. to 92.48 p. c.
Oil from Hokkaido	0.8989	—36.55°	1.4590	2.7 „	6.57 „	75.92 „	82.49 „

As a result of the investigations it appears that the peppermint oil obtained in Japan from foreign varieties excels the native product in pleasant odour and taste. Since it is not to be expected that the English and German varieties will gradually acquire the properties of the Japanese peppermint, the cultivation of these foreign kinds may be profitable.

The method pursued in Japan for the winning of menthol (freezing out) might be improved. The product from Japan designated as menthol-free oil, still contains 34 to 44 per cent. menthol; this latter is extracted in Germany, and the residue is put upon the market as dementholised peppermint oil.

Most of the peppermint oils, which in the course of the past report-year, were laid before us for judgment, were adulterated, in which adulterations phthalic ester and glycerin acetate repeatedly played the chief rôle; so that what was said in our last *Report* (pp. 38 to 40) would have to be repeated in the main, if we wished to enter into the details of our investigations. Here also the adulterations were chiefly recognised by the far too high ester number. Phthalic ester was used in comparatively small quantities; on the contrary, additions up to about 33 per cent. were proved present in the oils adulterated with glycerin acetate. A peppermint oil treated with the exceedingly easily soluble glycerin acetate, ought to be very soluble, and it is significant of quality of the peppermint oil used as "basis", when an oil containing about 30 per cent. glycerin acetate did not completely dissolve in 10 volumes of 70 per cent. alcohol, as was the case with one sample.

A new kind of adulterant was observed in a peppermint oil which had been treated with phthalic ester. Apparently an effort had been made to improve the low menthol content and for this purpose amylalcohol had apparently been used. Unfortunately we were unable to establish its presence absolutely, since the sample at our disposal was very small. They had not been very moderate in the use of this adulterant, for

the acetylation value was thereby so increased, that an apparent menthol content of 89.3 per cent. resulted, *i. e.*, an amount, which even in normal (unseparated) Japanese peppermint oil — which does not come into account here, — belongs to the exceptions.

Two other samples, which were likewise offered as good cheap goods consisted wholly or at least partly of waste products, such as are obtained in the rectification of Japanese peppermint oil. The low quality shows itself especially in the low menthol content and the absolutely unsatisfactory solubility, not to mention the deviations in the constants and the change in odour.

	I.	II.
$d_{15°}$	0.8563	0.8926
α_D	— 54° 34′	— 33° 56′
Solubility in 70 per cent. alcohol	insoluble	insoluble
„ „ 80 „ „ „	„	soluble in 1.5 vols., cloudiness on further addition
„ „ 90 „ „ „	sol. in 3 vols.	—
Saponification value	7.0	15.3
Ester value after acetylation	43.1	108.5
Total menthol	12.4 per cent.	32.9 per cent.

Only last year we gave a few details over the occurrence and the combating of the peppermint rust, *Puccinia Menthæ*, Pers. Since this dangerous rust disease has made itself noticeable for some time in various districts in which peppermint is cultivated the communications of G. Korff[1]) about this disease maybe of interest.

The peppermint rust attacks not only the cultivated *Mentha* species, but also wild-growing, and has been found on *M. arvensis*, *M. aquatica*, L. and *M. viridis*, L., as well as amongst the genera *Calamintha*, *Melissa*, *Melittis*, *Nepeta* and *Satureja*. According to the investigations of Cruchet[2]), with the rust fungi appearing on the *Mentha* species, it is a case of various forms of *Puccinia Menthæ* suitable to the species in question, which forms only engender the rust discase on plants of similar kind. Since it is still uncertain whether the autœcic[3]) fungus as such winters inside the plant, or whether a new infection, caused by spores that have survived the winter, happens yearly, the spreading and overwintering of *Puccinia Menthæ* should be everywhere carefully observed whenever there is an opportunity. Plants suffering from unfavourable conditions of growth are the most suitable victims of the peppermint rust. Hence in laying out a peppermint plantation, it is well to see that all conditions favourable for a good development of the plants are fulfilled. In addition to a suitable climate and good soil, the peppermint plant needs a suitable manure vich in potash and phosphates, but not over-rich in nitrogenous substances[4]).

Oil of Perilla citriodora. — The labiata *Perilla citriodora*, Makino[5]) discovered a few years ago near Tokio resembles much in appearance the *P. ocymoides*, L., but differs from the variety named, however, in the smell of lemongrass oil which its leaves develop when rubbed. Kondo and S. Yamaguchi[6]) were able to obtain from the dried plant 2 to 3 per cent. of an essential oil of specific gravity 0.911 to 0.913. The oil contained 59.26 per cent. of citral. The oil remaining after separating the citral

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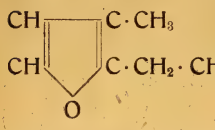
[1]) *Heil- und Gewürzpflanzen* **2** (1918/1919), 265. — [2]) *Zentralbl. f. Bakteriol. u. Parasitenk. Abt.* II. **1906**, 212. — [3]) The various spore forms appear on the one and the same plant which nourishes them. — [4]) Cf. *Reports* October **1912**, 91; **1917**, 36. — [5]) The plant has up to 1910 not been mentioned in the *Index Kewensis*. — [6]) *Pharm. Soc. Japan* **446** (1919), 263. According to *Journ. chem. Soc.* **116** (1919), 492 and *Parfum. moderne* **12** (1919), 148.

was fractionated under a pressure of 25 mm.; from fraction passing over at 90 to 100° (49 per cent. of the citral-free portion) a new body was isolated which had the empirical formula $C_{10}H_{14}O$ and was named perillene[1]). Perillene (b. p. 185 to 186°, d 0.9017, α_D 0°, $n_{D21°}$ 1.4705) is a colourless pleasant-smelling fluid, which becomes gradually brown and probably has the constitutional formula here given.



Perillene assumes a purple-red coloration with bromine, which coloration changes rapidly to green. A dihydroperillene was obtained by reduction (b. p. 182°, $d_{22°}$ 0.8852, $n_{D22°}$ 1.4576). From the further fractions (100 to 120°, 5 per cent.; 120 to 130°, 9 per cent.; above 130°, 6 per cent.; residue, 31 per cent.) another compound could be isolated, characterised by the following constants: — b. p. 251°, $d_{11°}$ 0.9088, $n_{D11°}$ 1.5018, $[\alpha]_D$ — 4.358°.

Pimento Leaf Oil. — *Re* pimento leaf oil, which a few years ago was examined by the Imperial Institute[2]), the same Institute again reports: The leaves of *Pimenta officinalis*, Lindl. *(Myrtaceæ)* from Jamaica yielded 2.9 per cent. of a bright yellow-brown oil on steam-distilling, of a pleasant odour, and had following properties: — $d_{15°}$ 1.055, α_D — 0.55°, n_D 1.534, phenol content 89 per cent. The oil is soluble in 1.1 parts of 70 per cent. alcohol. The phenols isolated from the oil had the boiling point 252 to 253° (755 mm.) and consisted almost entirely of eugenol. With its good quality and high phenol content of the oil, it should find a ready sale for the preparation of eugenol, isoeugenol and vanillin. A firm offered 14 s. per lb., the same price as was formerly paid for pimento oil[3]).

Pine-needle Oils. One must reckon with a complete failure of the pine-needle oil of Siberia — one of our most important raw materials before the war — on account of conditions in Russia; and it is not yet to be seen whether one can reckon on this article ever being imported again.

Silver-Fir Oil was delivered by Thuringia and the Black Forest in sufficient quantities; but the prices have reached such a height during to the dearth, that its employment for numberless purposes is out of the question.

The production of *Knee-Pine oil (Pinus Pumilio)* has been more satisfactory lately, for a number of new producers, encouraged by the high prices, have appeared in various districts who have laid themselves out for the delivery of large quantities.

Fir-cone Oil (Ol. Templinum) came from Switzerland in sufficient quantities, but at very high prices on account of the rate of exchange; there in however a large circle of buyers, who still use it in spite of its high price.

A few small trustworthy lots of *Pine-needle oil* again recently came from Thuringia; and there are still hopes that the *Ol. pini silvestris* which one has done without for so long, can again be regularly delivered.

Neither in the German, nor yet in the exactly similar Swedish pine-needle oils, both of which come from *Pinus silvestris*, L., has up to the present the nature of the contained ester been exactly determined. The supposition that bornyl acetate[4]) was present was confirmed by a thorough investigation of Thor Ekecrantz[5]). Ekecrantz

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[1]) The designation "perillene" is deceptive since it leads one to the conclusion that it is a hydrocarbon, instead of a furfuran derivative. Probably Kondo named the substance "perillone", which has become perillene through a printer's error. Cf. the designation of Semmler "Carlina oxide" for a similarly constituted constituent of carlene thistle oil, *Report* April **1906**, 15; Oct. **1909**, 36. — [2]) Cf. *Report* April **1914**, 83. — [3]) *Bull. Imp. Inst.* **17** (1919), 297. — [4]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 124. — [5]) *Medd. Kgl. Vetenskaps akad. Nobelinst.* **5** (1919) 1. As per *Chem. Zentralbl.* **1919**, III. 380.

examined a pine-needle oil from Boras in Sweden, with an ester content of 5.15 per cent., and a specific gravity 0.879. Amongst the acids he only ascertained the presence of acetic acid by means of the silver salt. The terpene alcohol was isolated from the fraction boiling at from 200 to 212° according to the process of Tchugayeff[1]) by means of magnesium methyl iodide, and was identified as *l*-borneol with a melting point of 203°. In the fractions boiling at from 190 to 200°, and from 212 to 225° could no other terpene alcohol be found. Accordingly the ester contained in pine-needle oil is *l*-bornyl acetate.

Oil of Pycnanthemum lanceolatum.—We can now enlarge upon the details *re* oil of *Pycnanthemum lanceolatum*, Pursh, given in our *Report* **1919**, 42, since the original work of E. R. Miller[2]) stands at our disposal. From the air-dried flowering plants *P. lanceolatum*. Pursh, collected in and around Madison, Wisconsin, Miller obtained by distillation 2.2 per cent. of a bright yellow oil with the following properties:—$d_{25°}$ 0.917, α_D — 4.6°, $n_{D16°}$ 1.4881. The oil contained nearly 19.2 per cent. terpene, which Miller estimated by repeated distillation of the oil with equal quantities of alcohol, and diluting of the distillate with much water. Miller himself acknowledges that this method does not permit of an exact estimation of the terpene.

The various components of the oil already mentioned by us were identified as follows:—Carvacrol by the nitrosocarvacrol, m. p. 152 to 153°, geraniol by the diphenylurethane m. p. 104°, the nitrolbenzylamine m. p. 105 to 106°, the nitrolpiperidide m. p. 140 to 141° (according to Wallach[3]) the nitrolbenzylamine has a m. p. of 109 to 110°, the nitrolpiperidide the m. p. 152°—accordingly the presence of dipentene cannot yet be regarded as absolutely certain), pulegone by the semicarbazone m. p. 169 to 170°, α-thujon?[4]) by the semicarbazone m. p. 175 to 176°.

Oil of Rue.—Two small test distillates obtained last year and this, from rue raised for experimental purposes in Miltitz, may not be passed over without mention, since they may be of some interest. The fresh flowering plant of *Ruta graveolens*, L., was used. The oils were of pale yellow colour and reacted as follows:—

	1919	1920
Yield	0.086 per cent.[5])	0.066 per cent.
$d_{15°}$	0.8492	0.8450
α_D	— 0° 43′	— 0° 40′
$n_{D20°}$	1.43386	1.43185
Solidifying (freezing) point	about — 4°	between — 6° and — 7°
Solubility in 70 per cent. alcohol	sol. in 4.5 vol.	sol. in 3 vol.
	with separation of paraffin.	

Part of the 1919 distilled oil was saponified, the acid value amounted to 1.5, the ester value 71.4. From the low solidifying point it is to be assumed that methylheptylketone prevailed amongst the ketones in both cases.

Re illnesses apparently caused by oil of rue B. Röntsch[6]) reports:—All the girls who had to cut the rue (*Ruta graveolens*, L.) in the Ferrein Medical Plantations south of Moscow fell ill during the harvest. In the course of two hours at the longest, the

[1]) *Berl. Berichte* **35** (1902) 3922. — [2]) *Circular* **2** (1918), Pharm. Exper. Stat., Univers. of Wisc. — [3]) *Liebig's Annalen* **252** (188), 125. — [4]) The presence of β-thujone is probable, but not absolutely certain. — [5]) The somewhat higher yield is perhaps explained by the fact that the herbs were already bearing fruit. — [6]) *Heil- und Gewürzpflanzen* **3** (1919), 149.

girls got swollen hands, swellings and strong itching on the arms and legs. Fever supervened with most, *viz.*, the younger girls, who remained incapable of work, some as long as ten days. In the first year the plants stood on manured, freshly broken meadow-land, and contained an extraordinarily high percentage of essential oil.

This announcement tells us nothing new; Kobert (*Lehrbuch der Intoxikationen*, 2. ed., vol. II, p. 530) and Zörnig (*Arzneidrogen*, part I, 1909, p. 164) have already pointed out that the plant, especially in the fresh condition, causes inflammations of the skin.

Rose Oil (Attar of Roses), Bulgarian.—This year's harvest is less than that of the previous year by about a fifth, and the total yield is estimated at about 1100 kilos. At the commencement a much more unfavourable result was expected, and one had to pay 3½ times the price of the flowers in 1919; only in course of preparation the oil yield proved to be exceedingly good in consequence of the more favourable weather conditions, so that finally the above-named quantity was reached. The cost price amounted to 22000 to 26000 levas the kilo, which in view of the rising in price of all Bulgarian land products, can still be regarded as comparatively cheap. In addition to the high costs, and bearing in mind the exchange, the average selling price amounted to M. 22000 per kilo. With such a fantastic price, there was no especial inclination to buy observable, and it needs no affirming that the consuming circles as a consequence, turned more to the artificially prepared attar of roses. Since direct traffic communication with Bulgaria has been re-established, special consignments turn up now and again in Germany, which are made use of to enhance the credit of the mark, and hence it was occasionally possible to buy smaller lots below the market price. Also unfortunately, numerous lots of poor value have naturally made an appearance, and the cool demands of certain Bulgarian producers for all kinds of adulterants, such as geraniol, citronellol, &c. call for extreme caution when buying.

A "rose"-bank has been established in Bulgaria with a capital of 4000000 francs. This, on account of the reciprocity of banking and trading enterprises, has its headquarters at Sofia. According to the prospectus of the bank, which is printed in Bulgarian, German and French, a fourth of the capital was subscribed by Bulgarian rose cultivators, and the remainder by financially interested parties[1]).

According to an English Note[2]) the falling in the price of rose oil in 1919 is ascribed to the circumstances that in France as well in America, the offers of Bulgarian rose oil are greater than the demands. During the War considerable quantities of rose oil were obtained in France from the *Rosa centifolia*, L. which is ordinarily used only for the preparation of rose water and rose pomade. After the raising of the blockade Bulgaria delivered large quantities of rose oil to U. S. A. in order to exchange it for food.

From the following statistics, which are taken from the report of a firm not specifically named, it is obvious the production of rose oil in Bulgaria has fallen very much since 1916.

Rose Oil Production in Bulgaria.

1915	1916	1917	1918	1919
3730 kg.	4100 kg.	3020 kg.	2560 kg.	1845 kg.

As in Spain and other countries, the population again devotes itself more to the kind of agriculture that pays, so in Bulgaria the people seem to be coming to the opinion that the cultivation of tobacco and cereals is more profitable than rose culture.

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[1]) *Perfum. Record* **10** (1919), 216. Cf. *Report* **1918**, 42. — [2]) *Chemist and Druggist* **92** (1920), 521.

At the present time it would be looked upon as a wonder, if we had not to report of flagrant adulterations of rose oil. Although only very small samples were at our disposal on account of the prevailing high prices, yet however, these mostly sufficed for us to recognise that the oils were adulterated, and we again observed palmarosa oil as well as spermaceti, also the same adulterants which we mentioned in our previous *Report*. p. 44. Consequently we will not go into further details, in order not to repeat what has already been said, but will rest satisfied with this hint, which should be enough to put every rose oil buyer on his guard.

Rose Culture in India. — Although the Indian rose industry has scarcely any significance in the commerce of the world, yet a few more explicit details about the rose cultures which have existed for two centuries in the district of Gazipur on the Ganges, north-east of Benares, will not be without interest. Gazipur was once the rose-garden of India; now the whole perfumery industry has gone back very considerably here, and the so-called Gazipur Rose Water partly comes from other parts of the province. According to a report of I. P. Srivastara[1]) who visited Gazipur in 1919, 96 acres in Pargana Gazipur and Thesil Gazipur are planted with roses, chiefly indeed with *Rosa damascena*, Mill. On a biggah of ground (1 biggah = 1600 sq. yds. = 1338 sq. m.) stand 2500 plants. After a year the young rose trees are transplanted from the nursery to the field, at the and of another year they bloom. The flowering time begins on "Sheoratri" (1st March), and ends on "Ram Naumi" (10th April), and only occurs once a year, not oftener, as in the district of Aligarh south-east of Delhi. During this period of 40 days, 46000 to 60000 blooms per biggah are gathered, roughly equal to 62 to 82 kg., *i. e.*, 463 to 613 kg. per hectare. In Bulgaria the yield of a good plantation is 4000 kg. per hectare[2]). This comparatively small result can only he ascribed to the carelessness of the farmers. On the one hand insufficient attention is paid to the manuring, on the other one attempts to gather repeated crops from the same plant for far too long a time, instead of replacing them by fresh ones. The roses are used almost exclusively for the preparation of rose water. Both the distillation apparatus, which is heated over a naked fire, and the whole manner of winning the product is very impracticable and uncleanly. Rose water is obtained in various strengths. Five thousand to forty thousand blooms are distilled each in two portions and give for the time being a yield of 25 to 32 quarts. The amount of raw material used has no influence on the quantity of the yield.

The process according to which rose oil is obtained in small quantities may now be mentioned. A very concentrated rose water is prepared by distilling five to six times with the same water continually fresh blooms, the quantity of blooms being increased each time. The concentrated water is allowed to stand overnight in a wide-mouthed vessel, covered with a cloth. In the early morning the oil, which has formed a thin layer on the surface of the water, is skimmed off with a duck's feather and collected in a bowl.

Rose extract Oil, German. — F. Elze obtained an oil from centifolias by means of an easily volatile solvent. It had the following properties: — Solidifying point +13°, $d_{20°}$ 0.9894, α + 0° 6′, acid value 3.15, ester value 2.9, ester value after acetylation 317.5. Together with phenylethylalcohol as chief constituent, geraniol (diphenylurethane, m.p. 81

[1]) *Perfum. Record* **10** (1919), 190. — [2]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 554.

to 82.5°), citronellol (naphthocinchoninic acid, m.p. 225° from citronellal), nerol (diphenylurethane, m. p. 50 to 50.5°) and farnesol could yet be identified, and accordingly the results of earlier investigations were confirmed[1]).

Oil of Roubieva multifida. — From *Roubieva multifida*, Moqu.[2]), a chenopodiacea growing wild in California, the W. J. Bush Citrus Products Company (National City, California) distilled an essential oil which was examined by E. K. Nelson[3]). The product was bright yellow, with an odour of aniseed and terpenes and had the following constants: — $d_{25°}^{25°}$ 0.8542, $[\alpha]_D$ + 35.75°. Sixty per cent. of the oil first distilled over at 37 to 40° (3 mm.). By repeated fractional distillation Nelson found that 85 per cent. of the product consisted of a terpene fraction, which after rectification over sodium had the following properties: — b. p. 169 to 171° (ordinary pressure), $d_{20°}^{20°}$ 0.8507, $[\alpha]_D$ + 46.4°. The fraction polymerised easily on warming, had on odour of phellandrene and formed a nitrosite m. p. 103 to 104°, according to which β-phellandrene was present. From the higher boiling component anethole was isolated. On distillation a resinous residue was left behend, probably polymerised phellandrene.

Sandalwood Oil, East Indian. — E. W. Cotton gives a series of statistical information *re* East Indian sandalwood and sandalwood oil in the recently published "Handbook of Commercial Information for India". In Mysore and Coorg all sandalwood trees are Government property. Private ownership is indeed recognised in Madras, but as a matter of fact the sandalwood production is practically a monopoly of the Forest Authorities. The amount obtained from the three provinces and offered for public sale amounted on an average to 2500 to 3000 tons on the year. To this must be added the needs of the native population for sandalwood which is estimated at 500 to 600 tons yearly. There were sold in Mysore

1908/09	2114 tons	of a value of	£ 70000
1911/12	2363 „	„ „ „	„ 84000
1912/13	2414 „	„ „ „	„ 151200

The price increase in the year 1912 was a result of German competition in the buying. As the Germans were absent in 1914 the sale had no success, and only at the next auction were 2000 tons sold at £ 113300 — as a consequence of American purchases — supposed to be partly on account of the Germans. When the auction took place in the following year, *i. e.* 1916, the factory in Bangalore had just been opened. Although only 1347 tons were disposed of by sale, a sum of £ 153300 was obtained, a sum from which resulted a considerable rising in the price of sandalwood oil on the London market. Since then the auctions ceased. The amounts of sandalwood sold in Madras, which are not more explicitly given, had 1913/14 a value of £ 10000, 1917/18 of £ 35000.

There were sold in Coorg

1914/15	32 tons	of a value	£ 1660
1915/16	380 „	„ „ „	„ 23330
1917/18	300 „	„ „ „	„ 35000

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[1]) *Chem. Ztg.* **43** (1919), 747. Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 566 to 570. — [2]) As per *Index Kewensis*. In the English Note "*Rubieva Multifida*" is written. — [3]) *Journ. Americ. chem. Soc.* **42** (1920), 1286.

Whilst the average price per ton of sandalwood was about £ 23 before 1912, it then rose to £ 60, in 1914 to £ 70 and in 1917 to £ 105 to £ 114.

The two factories erected in Bangalore had up to 31st December 1918 together treated 2113 tons of sandalwood and prepared 212371 lbs. oil. 196000 lbs. of this were sold, which brought to the state of Mysore in the year 1917/18 £ 183300.

The following compilation gives a view of the value of the exports of sandalwood and sandalwood oil since 1913:—

	Value of sandalwood	Sandalwood oil
1913/14	£ 128626	—
1914/15	„ 35918	—
1915/16	„ 103705	—
1916/17	„ 130351	£ 54823[1])
1917/18	„ 52347	„ 145713
1918/19	„ 10529	„ 227563

Formerly the most important exporting ports for sandalwood were Mangalore, Tellicherry, Calicut and Cochin. Now the oil is generally exported from Madras, Mangalore, Calcutta and Bombay.

The following tables show to what extent the trade in sandalwood, and the sandalwood oil industry have changed since the war.

Export of Sandalwood in year 1913/14

Destination	Amounts in percentage
Germany	43.4 per cent.
Great Britain	21.7 „ „
U. S. A.	15.5 „ „
France	7.7 „ „
Holland	3.1 „ „
Ceylon	0.4 „ „
Egypt	3.8 „ „
Japan	0.3 „ „

Export of Sandalwood oil in year 1918/19

Destination	Amount	Value
Great Britain	10151 gall.	£ 155013
Japan	4231 „	„ 61986
France	374 „	„ 7284
Hongkong	87 „	„ 1588
Egypt	48 „	„ 859
Java	59 „	„ 190
Australia	23 „	„ 463
Other countries	12 „	„ 180
Total:	14985 gall.	£ 227563

Six years ago B. J. Sham Rao[2]) had commenced to plant sandalwood trees in the Central Province of East India near Berar. The trees were raised from Mysore seed in shadowy and protected places, and developed very well, without great expense of maintenance. The wood was scarcely distinguished from Mysore sandalwood in smell and build, and it is to be expected that it also will yield a good oil.

A satisfactory explanation of the appearence of the spike disease on the sandalwood trees could not up to the present be found. Butler[3]) assumed that a poison is present in the sap; later, a connection between the occurrence of certain rust fungi on the *Lantana*-shrubs and the appearence of the disease, seemed capable of confirmation[4]). A. B. Jackson[5]) recently gave some information in the "Indian Forester", which perhaps touches the true origin of the disease. Up to the present neither fungus nor insect has been found as originator of the disease. Spike generally appears, where the sandalwood plants stand thickly on the ground, often at a great distance from the next infected area. Since the sandalwood tree may be a root parasite, which

[1]) The Calcutta values are wanting. — [2]) *The Indian Forester*. According to *Perfum. Record* **11** (1920), 66. — [3]) Cf. *Report* Oct. **1903**, 61. — [4]) Cf. *Report* Oct. **1913**, 95. — [5]) *Perfum. Record* **11** (1920), 32.

also lives parasitically on its own kind, this symbiosis of sandal on sandal might be able to cause an unnatural, unbalanced sap circulation and with this the commencement of the disease.

Sandalwood Oil, West Australian. — As stock plants of West Australian sandalwood stand *Fusanus spicatus*, R. Br. (*Santalum cygnorum*, Miq.) and at least 3 closely related *Santalum* species, viz. *Santalum lanceolatum*, *S. acuminatum* and *S. persicarium*[1]). J. L. Stoward[2]), Government Botanist and Plant Pathologist for Western Australia, has once more established that *Fusanus spicatus* and *Santalum cygnorum* are synonymous descriptions. The species *Fusanus* set up by Robert Brown was later coupled with the species *Santalum* by De Candolle. The differences of both species are so insignificant, that they may be regarded as identical. Engler[3]) also writes: "Certain varieties of the *Osyridœ*, as for example *Acanthosyris*, *Comandra*, *Santalum*, *Fusanus*, *Colpoon* and even *Osyris*, can all be grouped together and be regarded as members of one family".

According to C. E. Lane-Poole[2]) West Australian sandalwood oil contains 75 to 80 per cent. santalol. Since however a small amount also of "sesquiterpene ethyl" is said to be present, the oil has not been accepted in the English and American Pharmacopœia. Experiments in the hospital at Perth and in others have shown that "sesquiterpene ethyl" is just as curative as the santalol contained in the oil. In order to satisfy the requirements of the Pharmacopœia, the "sesquiterpene ethyl" has been separated from the oil by a special process, and a product equal to the East Indian sandalwood oil has been placed upon the market.

The consumption of West Australian sandalwood is great. It cannot be said whether it is used exclusively for perfumery, as carving wood, and for ceremonial purposes, or partly also for the production of "East Indian" sandalwood oil.

In the settled districts of West Australia the occurrence of sandalwood decreases. At present it is obtained in great part in the districts of the eastern gold fields. The sandalwood tree is also found in the interior of the continent near the Trans-Australian Railway.

According to the *Report of the Forest Department of Western Australia*[4]) the export of sandalwood, of £ 117072 in value, had attained an extraordinarily high level in the period 1st July 1918 to 30th June 1919. Since 1882, in which year the export of sandalwood brought in £ 96050, has no such turnover been attained. A ton of wood now costing £ 13, was at that time valued at £ 10. The getting of the wood has up to now brought no great profit to the inhabitants, but has been very profitable to the Chinese merchants who resold it in their own country.

Last year about 3720 lbs. of West Australian sandalwood oil are said to have been distilled. Although not yet accepted in the Pharmacopœia, the oil found a good market in Australia and Java and universal recognition. In medicine it was actually preferred to the genuine sandalwood oil, since it had no harmful secondary effects. The constitution of the alcohol generally designated as santalol, and which perhaps is an isomer of santalol, has yet to be investigated.

Sassafras Oil. — With a liniment of sassafras oil and petrolatum (1 + 25) good results were obtained in cases of poisoning with smack[5]).

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 350; *Report* **1918**, 43. — [2]) *Bull. Imp. Inst.* **17** (1919), 109. — [3]) Engler-Prantl, *Natürliche Pflanzenfamilien*, 3. vol., 1. part, p. 212. — [4]) *Perfum. Record* **11** (1920), 88. — [5]) *Eclectic Med. Journ.* **75** (1915), 70. As per *Digest of Comments on the Pharmacopœia of U. S. A. for* **1915**, 351.

Savin Oil. — In a work by E. Perrot and Mougin on *Juniperus Sabina*, L. and other *Juniperus* species the following observation occurs: — "It would be interesting to learn if *Juniperus thurifera*, L. is not collected in Spain and Algiers as savin, as for example *J. thurifera* var. *gallica* De Coincy in South France[1]). According to an English report[2]) *Juniperus thurifera*, L. is now known in Spain under the names *Sabina Alba* or *S. Roma* and appears to be used for oil-winning. The oil distilled from this plant had an odour like savin, but weaker, and possessed the following characteristics: — d 0.862, $\alpha + 61°$, ester content 4.8 per cent. The oil consisted chiefly of terpenes. The oil of *J. thurifera* var. *gallica* De Coincy, which Schimmel & Co.[3]) investigated years ago, had a higher specific gravity ($d_{15°}$ 0.9246) and a considerably less rotation (α_D between + 1 and 2°) than the Spanish oil.

Spearmint Oil. — The prices for American oil have indeed sunk to about $ 8 per lb. during this year, but the demand in the European market has considerably weakened on account of the high price. For many preparations in which spearmint oil was used the question of price is prohibitive.

Spearmint Oil, South African. — The *Mentha longifolia*, Huds. var. *undulata*, Briq. grown side by side with the *Mentha spicata*, Huds. in Germany appears to be cultivated also in South Africa. A short time ago the Imperial Institute[4]) examined a sample of *Mentha longifolia*, Huds. from South Africa; the leaves of which yielded 2.4 per cent. essential oil on distillation which was equivalent to 0.98 per cent. of the whole dried plant. The liquid colourless product of distillation possessed the characteristic odour and taste of spearmint oil. A chemical examination showed that it was similar to English and American spearmint oil with the exception of a larger amount of ketones, and that doubtless it would be saleable as spearmint oil.

Star anise Oil. — Although the export of star anise and cassia oil from China is under the control of the British Government, as we already announced last year[5]), adulterations with fatty oil occasionally occur. Such adulterations were possible so long as only a tenth of the oil coming from Hong Kong was exported by the authorities, which was the case up to now. Measures have been taken in the meantime to place the whole of the star anise and cassia oil under the control of the Government. It is to be expected that in future only unadulterated qualities will leave the country[6]).

Tea Oil. — From the formerly described oil from freshly fermented tea-leaves[7]), van Romburgh isolated β,γ-hexenol $CH_3 \cdot CH_2CH : CHCH_2CH_2OH$, which on oxidising with permanganate yielded propionic acid, and with chromic acid a hexylene acid, and also an α-naphthylurethane (m. p. 80°). The silver salt of the acid phthalic acid ester melted in the neighbourhood of 140°, the absorption of bromine amounted to 70 per cent. of the theory. β,γ-Hexenol is identical with the alcohol[8]) found by Schimmel & Co. in Japanese peppermint oil; the mixture of naphthylurethane and the silver salt showed no lowering of the melting point[9]).

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[1]) Concerning savin and the botanical species of *Juniperus* yielding the commercial drug see *Bull. des Sciences pharmacologiques* No. 2. Cf. *Report* April **1907**, 93. — [2]) *Perfum. Record* **10** (1919), 258. — [3]) *Report* April **1907**, 93. — [4]) *S. Afr. J. Ind.*, January **1919**. According to *Journ. Soc. chem. Industry* **38** (1919), R. 143. The publications containing the investigations of the Imperial Instiute were unobtainable, since the volume is out of print. — [5]) Cf. *Report* **1919**, 49. — [6]) *Perfum. Record* **10** (1919), 187. — [7]) Cf. *Reports* April **1897**, 39; April **1898**, 50. — [8]) *Report* **1918**, 39. — [9]) *Konikl. Akad. van Wetensch. Amsterdam, Wisk. en Natk. Afd.* **28** (1910), 83. As per *Chem. Zentralbl.* **1920**, I. 83.

The melting points given for hexylene-α-naphthylurethane and for the silver salts of the hexylene phthalic ester acids by van Romburgh do not agree with ours. Hence both preparations were again made by us, and each was recrystallised 4 times. The melting points also here did not vary considerably from those before found; hexylene-α-naphthylurethane, m. p. 71 to 72° (formerly 70 to 71°), from petrol ether, hexylene phthalic ester acid silver salt, m. p. 127 to 128° (formerly 126°) from alcohol.

Turpentine Oil.—The concern known as the "Naval stores"[1]) uses annually more oil of turpentine and resin than the present pinewood resources of America, can give without injury, according to the present process of obtaining them. According to Schorger[2]) 31 per cent. more turpentine oil and 36 per cent. more resin could be obtained at each harvest, if the number of "chippings" per season was doubled. Under the "cup and gutter" system now in use, the "chipping" is begun in the spring, *i. e.*, each week a row of cuts one inch in depth is made in the bark and sap-wood on the two inch wide "face" with a special hatchet. Whilst the rows were formerly half-an-inch from each other, they are now cut at 1/4 in. distances twice a week according to Schorger's process. In this manner the same surface receives in the same time double the number of "chippings" as formerly.

In this way Schorger obtained after the first year an extra yield of $ 450 per crop (1 crop is the yield of 10000 faces, on each tree are 2 faces at most). Otherwise with "narrow chippings"—*i. e.*, the single number of "chippings" were made so closely to each other that the resin-yielding surfaces only took up half the height—17.5 per cent. less turpentine oil and resin was obtained than with the usual procedure.

The Douglas pines—present in 4 species—belong to the most valuable and most widely distributed pine woods of North West America. Among them many gigantic old trees are found, often with twisted trunk, which shows hollows and scars filled with pitch a few inches above the ground. According to an American report[3]), a company—the "Northwestern Turpentine Co."—has commenced in a small way to collect and work the pitch of these "pitch-trees". The raw product, which is forwarded to Portland in casks for further manufacture, contains 25 per cent. turpentine oil and 70 per cent. colophony. It is hoped that a small quantity of balsam will be obtained.

Our last communication *re* rosin- and turpentine-winning in the Punjab is amplified by a report of this industry in the *Indian Munitions Board Handbook*[4]). At the present time only a *Pinus* variety, "chir[5]) of the Himalays", is tapped, which covers about 1500 English square miles in the State forests, and 1800 Eng. sq. ml. in the non-Government districts of the "United Provinces" and the Punjab. Moreover the winning of rosin could still be extended to the blue Himalaya pine[6]) and to the varieties growing in Assam and Burma, and the yield considerably increased. The Forest Authorities have two factories in Bhiwani (United Provinces) and in Jallo (Punjab). Apart from the trade with China, Java and other countries, the demand in India itself continually increases; the Indian rosin industry has now the chance of increasing by leaps and bounds.

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[1]) Cf. *Report* **1916**, 56. — [2]) *Bulletin* No. **567**. U. S. A. Department of Agriculture. — [3]) *Chem. and metallurg. Engineering* **22** (1920), 853. — [4]) *Pinus longifolia*, Roxb. (Commercial guide to the forest economic products of India. Calcutta **1912**). — [5]) Probably *Pinus excelsa*, Wall, known as the "Indian blue pine" is meant. — [6]) *Journ. Ind. and Eng. Chemistry* **10** (1918), 747.

A Japanese turpentine obtained from *Pinus Thunbergii*, Parl.[1]), a silver- or spruce-fir species known in Japan as *"Kuromatsu"* or *"Omatsu"*, contained, according to Y. Shinosaki[2]), 22,92 per cent. essential oil, 73.36 per cent. colophony, 3.61 per cent. water, and 0.21 per cent. impurities. The essential oil had the following properties: — $d^{15°}_{4°}$ 0.8740, α_D — 19.17°, $n_{D20°}$ 1.4738, acid value 0.53. It was soluble in 8 vols. 90 per cent. alcohol and in 28 vols. 80 per cent. alcohol. About 80 per cent. of the oil distilled over between 154 and 169°, and about 4 per cent. between 169 and 252°. The fraction boiling above 252° (15 per cent.) had the constants: — d 0.9244, α_D + 36.25°, $n_{D20°}$ 1.4993. On distilling *in vacuo* 3 chief fractions were obtained. The 1st fraction (73 per cent.) consisted of *d*-α-pinene together with a small amount of inactive pinene. The 2nd fraction contained camphene and the third a fluid tricyclic sesquiterpene with the constants: — b. p. 105 to 106° (2 mm.), $d_{15°}$ 0.9370, α_D + 43.5°, $n_{D20°}$ 1.5055. The reduction of the sesquiterpene gave a dihydrosesquiterpene with following characteristics: — b. p. 98 to 99° (2.3 mm.), $d_{15°}$ 0.9294, $n_{D20°}$ 1.4959, molecular refractivity 64.34 (reckoned for $C_{15}H_{24}$ mol. refr. 64.24).

E. Münch[3]) has published a work on the scientific principles of pine rosin produce, in which he discusses the methods of investigation, build and arrangement of the resin ducts, the formation of balsam and all questions touching upon this process, also the extent of the rosin yield and its dependance on vegetation conditions. The following important conclusions of this treatise may be mentioned: —

The resin ducts are generally filled to such an extent that the secreting cells appear compressed to a narrow lining of the resinous ducts. When wounded, the lining cells swell by absorption of water till the duct is completely filled. The size of the resin ducts increases in proceeding from the interior to the exterior of the trunk. At all points of crossing there is an open junction of the longitudinal and lateral ducts, so that the balsam movement is possible over wide tracts in the tree. When wounded the resin ducts increase in the new year's ring many times. The number of longitudinal ducts depends on the width of the year's ring. A connection between the number of resin ducts and the capability of yielding resin by single trunks was not to be demonstrated. A cubic meter of pine wood with a one-mm.-thickness of year's ring including the lateral ducts has about 4 litres of balsam.

The maximum possible yield of an incision is only obtained after waiting from 8 to 14 days, and longer. Shallow incisions yielded in the spring and with short intervals more resin than cuts of 1 cm. depth. On the other hand, in late summer and in spring deeper cuts with longer pauses yielded a greater supply. To make 2 cuts simultaneously one above the other on the same trunk serves no useful purpose, and in the long run does not raise the resin yield of the trunk[4]). The resin yield increases with the breadth of the face.

After the first incision if deep, a great decrease appears in the yield of resin, which, however, does not appear if a 3 or 4 weeks' pause intervenes after the first incision. Whether the grooves are arranged above each other or below each other or whether the cuts are continued downwards without interruption has no influence on the resin yield. The German process is recommended as the best. Standing room, crown and root development influence the yield of resin. 1000 to 1250 kg. resin per

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[1]) Cf. *Report* April 1913, 104. — [2]) *Journ. chem. Ind. Tokyo* 21 (1918), 763; 22 (1919), 451. As per *Journ. Soc. chem. Ind.* 38 (1919), A 21; A 877. — [3]) *Arb. aus der Biolog. Reichsanstalt f. Land- u. Forstwirtsch. Berlin-Dahlem* 10 (1919), 1. As per *Angew. Botanik* 2 (1920), 76. — [4]) Cf. also the announcement by Schorger on turpentine winning p. 56 of this *Report*.

hectare are annually obtained. High temperatures appear to influence the formation of resin satisfactorily, if after warm weather a period of rain sets in. Want of rain and dryness of air have an unsatisfactory effect.

Oil of turpentine has strong antiseptic properties. It calls forth the phagocytes and is a good remedy for infected wounds and peritonitis[1]). It is further recommended as a good remedy against lice[2]).

Re a further improvement in the oil of turpentine treatment[3]) of urinary diseases W. Karo[4]) reports since be used turpentine oil free from resin and oxidation products neither fever nor infiltration appeared after the injection. Karo dissolved quinine in oil of turpentine *(terpichin)* and had better results with this than with the eucupine-turpentine-remedy.

Re Indian turpentine and turpentine oil see p. 127 of this *Report*.

Wintergreen Oil.—Experiments on dogs with methyl salicylate showed that the ester brought about a strong hyperemia of brain and lungs[5]).

Wormseed Oil, American.—Up till now wormseed oil was only distilled in the neighbourhood of Baltimore from the whole wild-growing planted or cultivated plant of *Chenopodium ambrosioides*, L. var. *anthelminticum*, Gray. According to Indian official reports *Chenopodium ambrosioides*[6]) is now cultivated in Assam, Bengal and South India. In the neighbourhood of Calcutta the chenopodiacea is found everywhere and is known by the names of *Ban bathera* or *Chalai*. The seeds of *Chenopodium anthelminticum*, Gray obtained from America have been planted experimentally in India. The flourishing plant of *Ch. ambrosioides* in Mungpoo near Darjeeling yielded seed which on the whole was very poor in oil. Better results might be obtained if the plant was treated as an annual and sown betimes in March. When the plants have become sufficiently large they are transplanted crosswise in rows, each 18 inches apart. The ground should be manured and often broken up at first. When the tips of the plants commence to brown it is best to cut down the whole plant and subject it to distillation. No information was given in the report on the oil itself[7]).

The demand for American wormseed oil, which has become one of the best remedies for worms, ever increases. In Carroll County, Maryland, the centre of this new industry, 7 distillation establishments are in work during the season.

In October 1919, E. K. Nelson[8]) procured from 5 similar works 7 genuine oil-samples in order to estimate the ascaridole content of the oils and find their physical constants. Nelson laid special stress on the fact that the directions given by us for the distillation (see p. 60 of this *Report*) were observed, since above 150° ascaridole undergoes a molecular change. With a pressure of 3 to 6 mm. Nelson was able to distill the ascaridole fraction at 115° and the terpene fraction at 80°.

When American wormseed oil is prepared strictly according to directions the residue remaining after fractionating is small. On the contrary if the oil is obtained

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[1]) *Americ. Drug.* **63** (1915), 296. *Americ. Journ. Clin. Med.* **22** (1915), 164. As per *Digest of Comments on the Pharmacopœia of U. S. A.* **1915**, 353. — [2]) *Journ. Trop. Med. and Hygiene* **18** (1915), 254. As per *Digest* **1915**, 353. — [3]) Cf. *Report* **1919**, 53. — [4]) *Therap. Halbmonatsh.* **33** (1919), 355. — [5]) *Arch. Pharmacol. Sper.* **22** (1916), 327. As per *Digest of Comments on the Pharmacopœia of U. S. A.* **1916**, 240. — [6]) Probably *Chenopodium ambrosioides*, L. is meant since *Ch. anthelminticum* especially mentioned in article. — [7]) *Perfum. Record* **10** (1919), 231. — [8]) *Journ. Americ. chem. Soc.* **42** (1920), 1204.

by steam distillation under reduced pressure and without observing necessary precautions, it has a low specific gravity, a poor ascaridole content and leaves behind a considerable distillation residue, which probably consists of decomposition products of ascaridole. In the samples collected by the author the greatest distillation residue amounted to only 2.3 per cent., on the contrary 8 oils distilled purposely under reduced steam-pressure left residues of 7 to 25 per cent. These residues appear partly to consist of glycolic substances which are soluble in water.

A simple process for testing the purity of ascaridole is according to Nelson as follows:—A few drops of this substance are placed upon a metal plate warmed to 250°. The purity of the ascaridole is judged according to the rapidity with which these drops take fire.

The seven samples collected in Carroll satisfied the demands of the American Pharmacopœia:— $d_{25°}^{25°}$ 0.9538 to 0.9792, $[\alpha]_D$ —3.6 to —6.5°, soluble in 8 vols. 70 per cent. alcohol, ascaridole content 60 to 77 per cent., distillation residue 0.9 to 2.3 per cent.

The oils also from Java and those over a year old from Brazil were normal. On the contrary the product obtained from wild *Chenopodium*-plants contained indeed the same constituents, but less ascaridole than the oil from Maryland.

Nelson further established that chenopodium oil in addition to *p*-cymene contains *l*-limonene (tetrabromide, m. p. 104 to 105°). A small amount of a nitrosite melting at 155° indicated the presence of α-terpinene although oxidation attempts brought no satisfactory proof of this terpene.

A searching botanical investigation has been published by E. H. Wirth[1]) over the chenopodiacea *Chenopodium ambrosioides* var. *anthelminticum* which yields the American wormseed Oil. The plant probably originating from tropical America, occurs in several well-known varieties in the south and west of U. S. A. The evil-smelling annual or perennial plant has strong branches and grows 30 to 100 cm. high. The most important plant for oil winning is the achenium, whose diameter with the calyx amounts to 1 to 2 mm. In a fresh state the fruits, which appear singly or in panicles, have a shiny green appearance; on drying they gradually become straw-coloured. A very thin fruit-envelope, consisting of an inner and outer skin, surrounds the lentil-shaped pitch-black, shining seeds, whose diameter amounts to 0.8 to 1.2 mm. There are numerous gland-hairs on the outer skin, the two largest thin-walled end cells of which contain the oil. With the aid of micro-chemical tests Wirth has shewn that the oil is present only in the hairs, and not in the seed itself, as was formerly assumed. Since the generally used reagents for micro-chemical identifications of essential oils such as alcannin, osmic acid, fuchsine and copper acetate solution were unusable, Wirth made use of a 50 per cent. solution of potassium hydroxide in 50 per cent. aldehyde-free alcohol. Brought into contact with this solution, the chenopodium oil became deep yellow on warming, then gradually deep-red, and finally red-brown. This reaction can also be well observed under the microscope with thin sections.

Whilst the stem of the plant has no gland hairs, yet they are found on both sides of the leaves, but smaller and less numerous than on the fruit. The ovaries are covered likewise with many similar oil-containing hairs.

The flowering plant has not, up to the present, been distilled. Such an experiment would probably bring light upon the question as to whether the cymene in ordinary wormseed oil was originally present, or whether it only originated from the ascaridole after the fruit had developed.

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[1]) *Journ. Americ. Pharm. Assoc.* 9 (1920), 127.

It is generally accepted that wormseed oil from Western America is not of such a good quality as the Baltimore oil. Wirth has thoroughly examined such a western oil[1]). He followed the directions given by Schimmel & Co. in distilling it (preparation of smaller quantities, shorter period of distillation, warm-running condenser)[2]). Only the finely divided fruits previously macerated with water were used for distillation. From 2 kg. of fruit, dried in sun or shade, 46 g., *viz.* 2 per cent. of oil could be distilled in 80 minutes. It had the following properties: — $d_{15.5^\circ}$ 0.9343, α_{D25° — 6.21°, n_{D40° 1.4690. The oil was soluble in 16 parts of 70 per cent. alcohol.

This oil was again distilled in steam; the first 70 to 75 per cent., and the last 25 to 30 per cent. were collected in separate receivers. Two to three per cent. of a non-volatile resinous mass remained as residue. The two fractions had the following constants: — $d_{15.5^\circ}$ 0.9085 and 1.0002, α_{D25° — 12.89° and — 4.09°.

From the sun-dried seeds an oil was obtained which was separated into three fractions under a pressure of 8 to 10 mm. 1st fraction, 55 to 65°, 35 per cent.; $d_{15.5^\circ}$ 0.9116; α_{D25° — 12.4; n_{D40° 1.4885. 2nd fraction, 65 to 79°, 14 per cent.; $d_{15.5^\circ}$ 0.949; α_{D28° — 7.4°; n_{D40° 1.4860. 3rd fraction, 80 to 102°, 45 per cent.; $d_{15.5^\circ}$ 1.005; α_{D25° — 3.16°; n_{D40° 1.4720. The 1st fraction contained *p*-cymene (*p*-*iso*propenylbenzoic acid m. p. 160°); the sylvestrene reaction (devised by Schimmel & Co. for Baltimore oil)[3]) could not be obtained. Chiefly in the second, but also in the 1st fraction, *d*-camphor (semicarbazone, m. p. 237°) was identified; ascaridole was identified in the second fraction by the characteristic reaction described by Schimmel & Co. and Nelson[3]). From other samples of oils Wirth established that ascaridole was present to 42 to 45 per cent. and cymene to 42 to 44 per cent.

Hence the Western wormseed oil is distinguished from the Baltimore oil by its small ascaridole content and its high cymene content. Some time previously Schimmel & Co. had fractionated several oils with abnormal physical constants, from which they arrived at these results: — Normal American oil (d_{15° 0.9708) contained 62 to 65 per cent. ascaridole and about 22 per cent. cymene; light oil (d_{15° 0.9426) contained only 45 to 50 per cent. and on the other hand 38 per cent. hydrocarbons[3]).

The investigations of chenopodium oil carried out by Schimmel & Co.[4]) and by Nelson[5]) were continued by M. C. Hall and H. C. Hamilton[6]). They were unable to prove the presence in large amount of a constituent with constant boiling point. The boiling point steadily rose in distilling under reduced pressure. The first portions were slightly tinged, the last became darker and darker and had finally an odour of turpentine. Whilst the ascaridole, apparently belonging to the less volatile constituents, irritated the alimentary canal, the more volatile constituents were less irritating but more anthelmintic than ascaridole.

Ascaridole is, as we have proved[7]), the most important and effective constituent of the oil.

The American wormseed oils sent to our laboratory last report year for examination were again, without exception, artificial products of the usual composition (eucalyptole, anethole, menthol, amylacetate). In addition the presence of citronellal was established

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[1]) *Journ. Americ. Pharm. Assoc.* **9** (1920), 127. — [2]) Cf. *Report* April **1908**, 112. — [3]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 362. — [4]) Cf. *Report* April **1908**, 114. — [5]) Cf. *Report* October **1911**, 98. — [6]) *Journ. Pharm. and Exp. Therapeutics* **11** (1918), 231. As per *Chem. Zentralbl.* **1919**, III. 1022. — [7]) *Reports* October **1906**, 81; April **1907**, 103; October **1907**, 99; April **1908**, 114; April **1901**, 121; October **1910**, 142; April **1911**, 121.

in one sample, which, as the smell of the mixture led us to believe, originated from Ceylon citronella oil. If the producer thought that he was more closely approaching the odour of the natural oil with this, he made a very great mistake; in addition it does not alter its inutility as a worm-remedy.

During the War the cases of sickness due to intestinal parasites increased greatly. According to H. Brüning, this sickness, especially "Oxyuriasis", is to be ascribed less to the lowering of the quality, and sameness of the food, than to uncleanliness, brought about by lack of soap, fuel, under-linen and bed linen. In an exhaustive treatise[1]) Brüning gives the ways and means of successfully fighting the chief varieties of intestinal parasites — tape-worms *(Tœnia)*, thread-worms *(Oxyuris)* and maw-worms *(Ascaris)*. According to this, no cure for worms can be effected until the kind of worm has been absolutely identified. The cure of oxyuriasis especially is not easy and only by the most painstaking following of the directions given by Brüning, can it be accomplished. As the thread-worms live in the upper part of the colon, in the cæcum, and as only occasionally the females crawl to the lowest parts of the rectum to lay their eggs, the mouth-therapeutics must be amplified by that of the anus. The patients must be kept absolutely clean. Further it should be noted that cases of thread-worms seldom remain confined to one member of a family. Santonine, naphthalene, *Gelonida Aluminii subacetici comp. c. Alum. sulf.* and enemas with suitable admixtures are recommended as remedies.

The cure for maw-worms is simpler. For medicines there are santonica, or the santonine obtained therefrom, and most important of all, the American wormseed oil. The fact that the dispensing of santonine is not always harmless, caused Brüning[2]) to resort more to the use of wormseed oil. Like him, Thelen, Ruland, Schmitz, Vervoort and many other authors were able again and again to confirm the good effects of this medicine as antiascaridic without any disagreeable consequences accompanying the cure. Many have successfully employed the oil in fighting against the thread-worms. Cases of poisoning have occurred when using wormseed oil, and it should hence be taken only in the smallest possible doses consonant with effectiveness. Therefore it it should be seen to that it remains In the body no longer than is necessary for an effective cure.

The treatment of maw-worms should be as follows for children: — At 7 a. m. a light breakfast; at 8 a. m. and also at 9 a. m. as many drops of wormseed oil as the age of the child in years — but never exceeding 10 per dose; at 11 a. m. a good dose of purgative, best of all 10 to 20 to 30 g. castor oil, according to the age of the child, or a corresponding dose of compound licorice powder or soothing powder. If up to 2 p. m. no evacuation has taken place, repeat the dose.

The intestinal worms of the horse (*Sclerostemum equinum*, Dnj.) are hard to disperse. Green vitriol and tartar emetic are of little use; the latter can even cause inflammation of the bowels. Oil of turpentine works much better. One dose (60 g. in a litre of olive oil) gets rid of 50 per cent. of the parasites. The American wormseed oil is very effective — given in quantities of 16 to 20 cc. it destroys over 95 per cent. of the worms. Half this quantity has little effect. Accordingly chenopodium oil is the best means for dealing with the intestinal parasites of the horse; oil of turpentine comes next[3]).

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[1]) *Mediz. Klinik* No. **11** and **47**, 1919, according to kindly forwarded special reprint. — [2]) Cf. *Report* October **1907**, 99. — [3]) Stall, Wilson and Wigdor, *Vet. Record* of 21. June **1919**. According to *Pharmaceutical Journ.* **103** (1919), 3.

Chenopodium oil can bring about kidney disturbances in rabbits fed exclusively on oats according to W. Salant and R. Bengis[1]), when administered either through the mouth or subcutaneously. A few fatty oils administered via the mouth had the same effect (*viz.*, cottonseed, olive, castor and coconut oils). If the rabbits have been fed on carrots, then even large quantities of oil have no effect. The effects of the chenopodium oil are said to be caused by the poorer nourishment of the kidneys in consequence of a lessened blood supply.

Re experiments with American wormseed oil and heart-exciting drugs on isolated frogs' hearts see reports of W. Salant and A. E. Livingston[2]).

A. J. Coutant[3]) reports a case of poisoning which happened in the treatment of hook-worm disease with American wormseed oil, and cites 12 further similar cases from the literature on the subject.

L.W. Scoville found chenopodium oil the least poisonous for animals when administered mixed with a fatty oil; administered in successive doses it had a double effect[4]).

The *Digest of Comments on the Pharmacopœia of U. S. A.* **1915**, p. 339 contains dissertations by Salant and Nelson *Concerning the toxic properties of wormseed oil*[5]) and of Motter *On the hook-worm sickness*[6]) which already have been discussed by us.

Xanthorrhœa resin Oils.—The origin of the acaroid resins which have been examined up to the present is according to Tschirch[7]) not yet absolutely ascertained. For the yellow resin *Xanthorrhœa hastilis*, R. Br., and for the red resin *X. Australis*, R. Br. are given as the plants from which they respectively originate. R. H. Rennie, W. T. Cooke and H. H. Finlayson[8]) assume that the resins mentioned[9]), in which benzoic, cinnamic, and *p*-cumaric acid free or as ester, vanillin and *p*-hydroxybenzaldehyde were found, originated from New South Wales. The authors themselves then examined resins which they had received from the Kangaroo Island, South Australia (a red resin of unknown origin and a yellow resin of *Xanthorrhœa Tateana*, F. v. Müll.), and from West Australia (a red resin of *Xanthorrhœa Preissii*, Endl.). The resin contained *p*-cumaric acid—free or as ester, and *p*-hydroxybenzaldehyde. On steam-distilling a strong alkaline solution of the red resin of unknown origin 0.35 to 0.36 per cent. of a solidifying essential oil was obtained, which could be recrystallized from alcohol (almost colourless sweet smelling needles of m. p. 49°) and proved to be identical with the pæonol $C_6H_3OCH_3^{[1]}OH^{[3]}\cdot CO\cdot CH_3^{[4]}$ contained in the oil of *Pæonia Moutan*, Sims. In addition the distillate contained a small amount of liquid with an odour of vanillin and traces of a higher melting body.

The yellow resin of *Xanthorrhœa Tateana* yielded by the same treatment considerably more distillation product (about 5 per cent.) which in addition to pæonol, and the other substances found in the red rosin contained hydroxypæonol $C_9H_{10}O_4$ (m. p. 79°; b. p. 185° [20 mm.]; about $^2/_3$ of the pæonol present). The hydroxypæonol is a colourless body, easily soluble in alkalies, which like pæonol gives a red-wine coloration with ferric chloride. Cold concentrated nitric acid gives a strong blue coloration which changes to blood-red, especially on warming, and which on boiling with concentrated

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[1]) *Journ. Pharm. and Exp. Therapeutics* **9** (1917), 529. According to *Digest of Comments on the Pharmacopœia of U. S. A. for* **1916**, 244. *Chem. Zentralbl.* **1919**, III. 934. — [2]) *Americ. Journ. Physiol.* **41** (1916), 21. According to *Digest for* **1916**, 244. — [3]) *Journ. Americ. Med. Ass.* **67** (1916), 1593. According to *Digest of Comments or* **1916**, 244. — [4]) *Bull. Pharm.* **1915**, 490. According to *Digest of Comments for* **1915**, 399. — [5]) *Report* October **1915**, 43. — [6]) *Report* April **1915**, 50. — [7]) A. Tschirch, *Die Harze und die Harzbehälter*, 2nd ed., p. 249. — [8]) *Journ. chem. Soc.* **117** (1920), 338. — [9]) Information as to source wanting. Schimmel & Co. found cinnamic acid in both resin oils, free and as ester, as well as styrene. Cf. *Report* October **1897**, 60.

nitric acid becomes permanent. If the red solution is diluted and made alkaline with sodium hydroxide, a dark-green coloration appears which is not absolutely permanent. The oxime (m. p. 107°) and the dimethyl ether (m. p. 102 to 103°) could be prepared, and the proof deduced that in hydroxypæonol there is a monomethyl ether of the 2,4,6-trihydroxyacetophenone present. The position of the methoxy group (probably the *para*-position, pæonol gives quite similar reactions) could not be decided however with certainty.

The red rosin of *Xanthorrhœa Preissii* was also dissolved in alkali and subjected to steam distillation. Slightly over 1 per cent. of a yellow strongly smelling oil passed over that at 20 mm. was separated into five fractions (110 to 155°, 155 to 165°, 165 to 185°, 185 to 200°, 200 to 210°). The small residue was somewhat viscous and uncrystallisable. Fraction 3 contained chiefly pæonol and a small quantity of a non-crystallising oil. Fraction 4 proved to be hydroxypæonol. Fraction 5 was solid and was recrystallised from alcohol (m. p. 69.5°). Probably a methoxydiphenyl ether was present, but an exact proof was not forthcoming. From fraction 1 a colourless oil was obtained by distillation 118 to 120° (20 mm.), whose identity with *l*-citronellol was established (silver salt of the citronellylphthalic ester acid; m. p. 125°). The higher fractions of the raw oil had a mint-like smell, and it is to be assumed that *iso*pulegol was present that had probably been formed from citronellal during the frequent distillations[1]).

Oil of Xanthoxylum ailanthoides.—Our note on the essential oil of the leaves of *Xanthoxylum ailanthoides,* Sieb. and Zucc. (*Report* October **1916**, 62) is amplified by the following information from Raspe & Co.[2]), Kobe. The rutacea grows wild in Suruga in Idzu, on the island Oshina in Idzu and on the Liukiu and Ogasawara Isles. In Ogasawara the plant in named *Ako.*

(*a*) Oil from old leaves (*Dshukuyo*-oil). Colour orange yellow, smell and taste pleasant somewhat piquant. Yield 0.5 per cent. Angle of Rotation is $\alpha_D + 6.35°$, not $\alpha_D - 6.35°$ as stated in *Journ. Soc. chem. Industry* **34** (1915), 1270[3]). B. p. 200 to 240° (ord. press). The oil formed many crystals on being shaken up with sodium bisulphite solution. On standing over night in ice-cupboard the whole formed a crystalline mass. The chief constituent methyl-*n*-nonylketone, was identified by the constants (b. p. about 232°; $d_{15°}$ 0.8302; freezing point 10°), and by the semicarbazone (m. p. 123°). At 14 mm. the five following fractions were obtained from oil treated with sodium bisulphite solution:— 65 to 80°, about 10 per cent. of the raw material, smell strongly of pinene; 80 to 90°, about 30 per cent. of the raw material, smelt strongly of ketone, and consisted mostly of methyl-*n*-nonyl ketone; 90 to 100°; 100 to 120° and 120 to 130°. Methyl-*n*-heptyl ketone appeared also to be present in the oil.

(*b*) Oil from partly old leaves *(Han-dshukuyo-yu).* Colour bright yellow; angle of rotation is $\alpha_D + 5.75°$, not $-5.75°$[3]). The ketone content was apparently greater than that of the oil from old leaves.

(*c*) Oil from fresh leaves *(Shinga-yu).* Colour yellowish-green, odour pleasanter than that of (*a*), and (*b*). Angle of rotation $\alpha_D + 6.63$, not $\alpha_D - 6.63$[3]).

Yamakosho leaf Oil.—Angle of rotation of this oil is $\alpha + 18.8°$[4]), not $\alpha - 18.8°$, as stated in *Journ. Soc. chem. Industry* **34** (1915), 7270[5]).

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[1]) Cf. *Report* April **1909**, 96. — [2]) Y. Shinosaki, *Report of the Industrial Laboratory (Kogyo Shikenjio) Tokyo,* March **1916**. *Yakugaku Zashi* **1906**, 1095. — [3]) Cf. *Report* **1916**, 62. — [4]) Y. Shinosaki, *Report of the Industrial Laboratory (Kogyo Shikenjio) Tokyo,* March **1916**. *Yakugaku Zashi* **1906**, 1095. — [5]) Cf. *Report* **1916**, 63.

Pharmacopœias.

French Pharmacopœia.

The French Pharmacopœia Commission has published this year a supplement to the edition of 1908, which on the one hand brings further details on properties and testing of freshly accepted preparations, and on the other, contains reports and amplifications of the text of various articles in the book. Fresh admissions of essential oils and related products have not resulted, on the contrary the up till now officially recognised apiole has been crossed out. Several alterations have been made, but not to the extent desired, according to our opinion. We reproduce them without further remark, and refer only to our earlier discussions of the Pharmacopœia, from which all else is self-explanatory[1]).

Aniseed Oil.—The specific gravity is valid for not 17°, but 20°.

Bergamot Oil.—α_D + 8 to + 22°.

Cinnamon Oil, Ceylon.—Correction of an error in the description of the aldehyde estimation.

Clove Oil.—$d_{15°}$ 1.050 to 1.068.

Juniper Berry Oil.—$d_{15°}$ 0.860 to 0.885.

Peppermint Oil.—Absolute freedom from colour is demanded.

Rose Oil.—The colour may also be greenish.

Sandalwood Oil.—Correcting a formula error in correcting the santalol content.

Terpin Hydrate.—Molecular weight not 180, but 190. Terpin hydrate is soluble in 280 parts of water at 15°, and in 6.9 parts of 95 per cent. alcohol at 10°.

Thyme Oil.—$d_{15°}$ 0.900 to 0.950.

Chemical Preparations and Drugs.

Benzaldehyde. We had already mentioned in our previous *Report* (p. 64) that the very perceptible scarcity in recent years of chlorine-free benzaldehyde had resulted in a "poor-in-chlorine" article being placed upon the market. Also a distinction was made between "poor-in-chlorine" and "traces of chlorine"; and proposals were further made to distinguish according to chlorine content, 3 qualities of benzaldehyde *viz.*, chlorine-free, up to 0.02 per cent. chlorine, and up to 0.2 per cent. chlorine. Meanwhile some people have gone so far as to substitute "technically chlorine-free" for "poor in chlorine", and to all appearances mean such benzaldehyde where the chlorine content does not exceed 0.02 per cent.

[1]) *Report* November 1908, 143.

Apparently there is not much worry over the chief difficulty, *viz.*, the accurate estimation of such small quantities of chlorine; at least, various benzaldehydes with guaranteed chlorine content, which arrived at our laboratory for examination, mostly contained very much more chlorine than was stated, as is seen from the following examples:—

Benzaldehyde	1.	Guaranteed	chlorine	content	0.02	per cent.;	found	0.42	per cent.		
„	2.	„	„	„	0.02	„	„	„	0.54	„	„
„	3.	„	„	„	0.002	„	„ [1]	„	0.23	„	„
„	4.	„	„	„	0.02	„	„	„	0.062	„	„

The causes of these differences are not clear to us. Perhaps it is a case of the benzaldehyde containing the impurity chlorinated partly in the nucleus, and partly in the side-chain, and probably it was only this latter that had been estimated. By our method however, the total chlorine was estimated; and the total chlorine content, is the important thing.

In a product sent to us as "technically chlorine-free" we found a chlorine-content of 0.08 per cent., an amount which gave such strong reactions even in the qualitative tests that we felt strongly inclined to describe the product as not coming up to the quality of even "technical".

It seems to us that one is on the wrong track here, and that this custom will lead to universal confusion, in which the honest trader will have all his trouble for nothing. If this nuisance—giving a misleading description—continues, it will end in all benzaldehyde being finally designated as chlorine-free, even when containing ever so much chlorinated compound. In the long run this condition becomes impossible. It is to be hoped that a return will soon be made to the good old principle of only distinguishing between truly chlorine-free and chlorine-containing benzaldehyde, and getting rid of all intermediate grades, for what was possible before the war, should be equally possible after. This would mean making it easier for trade, as every disinterested thoughtful person will readily admit; for a qualitative test is performed much more rapidly than a quantitative one, which is of very great importance; for quick decisions are generally necessary in buying at sales. As experience moreover points out, how many come to absolutely false results in the quantitative estimation of the chlorine in benzaldehyde (whether this is due to the way the experiment is carried out, or whether to the method of estimation, is of secondary importance), and as the quality of a benzaldehyde can with a little practice be very well determined by a qualitative test, so is this one more reason for us taking up the standpoint just expressed.

This view, of course, does not prevent us from making the way easier for the quantitative estimation of benzaldehyde. Already in our last *Report* we brought forward a method (boiling with alcoholic potash) with which good results are obtainable, but the chief drawback of which is that only the side-chain chlorine can be estimated. What is of importance, however, in such an estimation, is that it is not a case of the position of the chlorine in the molecule; and meanwhile we have persued our investigations in this direction. Earlier quantitative estimations[2]), brought forward by us on the occasion of a dispute, will not be taken up again this time, for then we estimated the chlorine in the nucleus and in the side chain separately and this method does not serve our present purpose. A method worked out by R. Benedikt and H. Zikes[3])

[1]) Probably due to a slip of the pen of the sender who probably wrote 0.002 instead of 0.02 the true value. — [2]) *Report* April 1891, 8. — [3]) *Chem. Ztg.* 18 (1894), 646.

for the estimation of small quantities of chlorine in fats seemed to us more suitable, in which the substance is burnt in a tube charged with lime and open at both ends as follows: — The substance enters one end slowly drop by drop, and simultaneously a current of air, or better still CO_2 is led through the tube. The method gives very good results, as the authors have shewn by using mixtures of known chlorine content, but it is rather troublesome and takes up too much time. We soon gave this method up, on finding a simpler one which gave just as good results. We have transformed our qualitative test to a quantitative one, by placing in a closed space (round flask of about 12 litres capacity), a weighed quantity of benzaldehyde, and then igniting. The benzaldehyde in placed in a small asbestos-wicked lamp, which is weighed before and after ignition, in order to determine the amount of benzaldehyde consumed. The disturbing effect of soot-development is reduced as much as possible by leading in oxygen; and escaping products of combustion pass into water. When combustion is complete, the flask is washed out with water, and the washings filtered along with the water which has taken up the escaping products of combustion, into an Erlenmeyer flask. In this way all the carbon particles are got rid of, and the filtrate contains the dissolved HCl, which is estimated by titrating with silver nitrate solution. Thus the total chlorine-content can be determined, whether in side-chain or nucleus, or in both. The experiment can be quickly performed and gives very good results, as benzaldehydes of known chlorine-content (in form of monochlorbenzene and benzyl chloride respectively added) have shewn us:—

Benzaldehyde	+ 1.0	per cent.	Cl;	found:	0.96	per cent.
„	+ 1.0	„	„	„	„	0.95	„	„
„	+ 0.2	„	„	„	„	0.18	„	„
„	+ 0.2	„	„	„	„	0.19	„	„
„	+ 0.2	„	„	„	„	0.21	„	„
„	+ 0.05	„	„	„	„	0.048	„	„
„	+ 0.05	„	„	„	„	0.051	„	„
„	+ 0.05	„	„	„	„	0.046	„	„
„	+ 0.02	„	„	„	„	0.015	„	„
„	+ 0.02	„	„	„	„	0.021	„	„

We have only given a rough sketch of the method, as we are still occupied in the working out of the apparatus. The publication is therefore only to be looked upon as a provisional announcement.

Benzyl alcohol.—Experiments with benzyl alcohol, benzaldehyde, and benzyl esters on worms showed that the alcohol with a concentration of 0.5 per cent. very quickly killed off earthworms; the aldehyde and the acetate are less effective. In cases of ascarides in pigs, and clinical cases (tape-worms) they had only a slight effect. It remains to be decided by further clinical tests as to the suitability of benzyl alcohol as a therapeutic agent[1]).

Re effect of benzyl alcohol on tubercle bacilli see p. 113 of this *Report*.

Re benzyl alcohol as a local anæsthetic see p. 113 of this *Report*.

Re sedative effects of benzyl benzoate on convulsions (spasms) see p. 113 of this *Report*.

[1]) *Journ. Pharm. and Exp. Therapeutics* **14** (1919) 323. As per *Chem. Zentralbl.* **1920**, I. 742.

Borneol. — As we announced before[1]), the Island of Hainan and South China are the two centres of production for Ngai-camphor, which is obtained from the composite *Blumea balsamifera*, D.C. In Burma also a *Blumea* species grows in great quantity, from which the natives prepare a camphor also. According to F. Mason[2]) the composite *Conyza grandis*, Wall. is the same as *Blumea grandis*, D.C. and *B. densiflora*, D.C. These plants do not yet appear to have been identified with certainty, as the Forest Department of Burma contemplates investigating more closely the origin and nature of the Burma camphor tree. It might easily turn out that it also is *Blumea balsamifera*, D.C.

The "Bureau of Science of the Philippine Islands"[3]) also gives a description of *Blumea balsamifera*, D.C., which is known to the natives as *Sambon* or *Gabnen*. The composite, which has an almost woody trunk, and grows to a height of 5 to 8 ft. is one of the commonest weeds of the Philippines.

Camphor. — Years ago we pointed out that both camphor and borneol are present in oil of sage[4]). Further we were able to point to *l*-camphor in a Syrian oil from *Salvia triloba*, L.[4]).

According to information from England[5]) the Californian varieties of sage, especially *Artemisia trifolium* ?[6]) also contain camphor, menthol, thujone, borneol, and thymol in varying quantities. The camphor and other constituents could be separated from one another by fractional distillation and freezing out. It is hoped to obtain large quantities of camphor in this way.

Further it is alleged that the Californian bay-tree, *Umbellularia californica*, Nutt. contains the same chemical substances. Up to now umbellulone as chief constituent, in quantities of 40 to 60 per cent., together with *l*-α-pinene, eugenol, methyleugenol and very little safrole are known to occur in Californian bay oil, but not camphor, menthol and thymol[7]).

E. K. Dorey[8]) gives following details *re* testing of raw Chinese camphor: 100 g. of a sample were pressed out; the difference of the moisture content of the original raw camphor and of the compressed residue is to be subtracted from the weight of the expressed fluid. From the figures obtained the true oil content can be calculated, on the assumption that the ratio of oil to water in uncompressed raw camphor was equal to ratio of oil to water in the expressed fluid.

K. W. Lane and O. F. Lubatti estimate the water content of raw camphor as follows: 5 g. raw camphor were placed in a glass tube of 25 mm. diameter, which is narrowed down to a tube of 4 mm. The latter is graduated and closed at the lower end. At the place where the tube is conically widened a piece of nickel wire gauze is placed, which provided with a little water, serves as a filter. For the estimation, 30 cc. of benzine were saturated with water, placed in the centrifugal apparatus and drawn off from the separated water. This benzine was then added to the camphor in the glass tube, and the whole was placed in the rotating centrifugal apparatus for several minutes. The

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 603; *Report* April **1914**, 107. — [2]) *Chemist and Druggist* **92** (1920), 425. — [3]) *Digest of Comments on the Pharmacopœia of U. S. A. for* **1915**, 210. — [4]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 458. — [5]) *Drug. and Chem. Markets* **6** (1920), 395. — [6]) An *"Artemisia tripolium (trifolium)"* has up till now not been known; probably the above mentioned *Salvia triloba*, L. is meant. — [7]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 485. — [8]) *Journ. Soc. chem. Industry* **39** (1920), 165.

whole of the water collected in the lower tube, from whose graduations the percentage content could be directly read off[1]).

Solubility of Camphor in Water.—After various experiments H. Leo and F. Rimbach[2]) found the solubility of camphor in Ringer solution = 1:577; in pure water 1:598. Since the solubility sinks with rising temperature, it is an exothermic reaction.

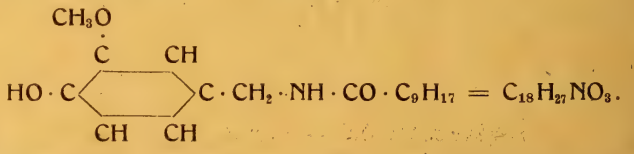
The estimation of dissolved camphor chemically, was successfully carried out by a process worked out by Tischner in the scientific laboratory of the firm E. Merck. The process is not described in the report.

Capsaicine.—The pungent constituent of Cayenne pepper, first isolated by Thresh[3]) and called "capsaicine", has been prepared in a pure state by E. K. Nelson[4]) and thoroughly examined. About 50 g. pure capsaicine $C_{18}H_{27}NO_3$, m. p. 65° were obtained according to Micko's procedure[5]) (starting with the ether extract), from 50 lbs. of a very strong Cayenne pepper. The alcoholic solution of the compound was optically inactive, but it crystallised in splendid plates, part of which were right-angled. In parallel polarised light the double refraction is strong.

By oxidising methylcapsaicine with alkaline permanganate Nelson obtained veratric acid $C_6H_3(CH_3O)_2^{[3,4]}\cdot COOH$, which allows us to presume the presence of a vanillin residue in capsaicine. This presumption was confirmed by the products which Nelson obtained by the hydrolysis of methylcapsaicine and of capsaicine with HCl:—Veratrylamine hydrochloride (3,4-dimethyloxybenzylaminohydrochloride) $C_6H_3(CH_3O)_2^{[3,4]}CH_2NH_2\cdot HCl$ and vanillylamine (4-hydroxy-3-methoxybenzylamine) $C_6H_3\cdot CH_3O^{[3]}\cdot OH^{[4]}\cdot CH_2\cdot NH_2$ (m.p. 132 to 133°)[6]). He also prepared the last base synthetically by reducing vanillinoxime; it is easily decomposed by caustic alkalies and hot water, but it can be preserved in the dry form if kept from light.

On hydrolysing capsaicine with alkali Nelson obtained a decylic acid, $C_{10}H_{18}O_2$, b. p. 258 to 261° (corrected), which on hydrogenating with colloidal palladium yielded, not capric acid, but an isomeric decylic acid. This decylic acid was not identical with that prepared by Wallach[7]) from menthone oxime and tetrahydrocarvo*iso*oxime.

By reason of these results, the elementary analysis, and the determination of the molecular weight, capsaicine can be regarded as a condensation product of vanillylamine and decylic acid, and formulated as follows:—



$= C_{18}H_{27}NO_3$.

The investigation of the constitution of capsaicine led E. K. Nelson[8]) to the synthesis of a number of other vanillylacylamides of the type $C_6H_3\cdot CH_2\cdot NH\cdot CO\cdot R^{[1]}\cdot OCH_3^{[3]}\cdot OH^{[4]}$. Vanillylamine suspended in ether and added to the corresponding acid chloride was the process used for preparation in most cases; only the acetyl and *iso*butyl derivatives were obtained from the anhydrides. In this manner Nelson prepared the vanillylamide

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[1]) *Journ. Soc. chem. Industry* **39** (1920), T. 50. — [2]) *Bioch. Zeitschrift* **95** (1919), 306. As per *Chem. Zentralbl.* **1919**, III. 562. — [3]) *Pharm. Journ. and Trans.* **7** (1876), 21. — [4]) *Journ. Americ. chem. Soc.* **41** (1919), 1115. — [5]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **1** (1898), 818. — [6]) In the original vanillylamine is indicated as **3**-hydroxy-**4**-methoxy benzylamine. Presumably it is merely a printer's error, since as a matter of fact, a vanillin but no **iso**vanillin derivative was present. — [7]) *Liebig's Annalen* **312** (1900), 204; 323 (1902), 325. — [8]) *Journ. Americ. chem. Soc.* **41** (1919), 2121.

of acetic, propionic, butyric, *iso*butyric, n-hexylic, n-heptylic, n-octylic, n-nonylic, n-decylic, n-undecylic, n-duodecylic, crotonic and benzoic acids. In the case of the homologous derivatives of the saturated fatty acids, the solubility in water decreases with rise in molecular weight, and *vice versa* in ether. The strength of the sharp taste reached a maximum with vanillyl-n-nonylamide and was equal to that of capsaicine. Zingerone, 4-hydroxy-3-methoxy-phenyl-methyl-ethyl-ketone, one of the pungent constituents of ginger, proved to be a thousand times weaker in taste than capsaicine.

Civet.—It is a well-known fact that civet is often adulterated, and this makes itself all the more uncomfortably felt, as the methods of examination are still somewhat incomplete, on account of the peculiar nature of this secretion, and hence admixtures often remain undetected. Adulterators seem to be especially active just now, for practically the whole of the samples examined in our laboratory during the last few months were adulterated. It will be well if we go into this subject a little deeper, for we can at the same time describe our method of examination, which deviates somewhat from the proceedure which was formerly recommended by others.

Dodge, A. Hébert[1]), E. Parry[2]), H. E. Burgess[3]) and E. Charabot (in cooperation with Hébert)[4]) have occupied themselves with the testing of civet. The civet was extracted with either a mixture of alcohol and ether (Hébert and Charabot), or with acetone and petrol ether successively (Dodge, Parry). The insoluble part of the civet in the solvents named, amounted to from about 3 to 5 per cent., any way always below 6 per cent., according to the observations of Hébert, and also of Parry. Three guaranteed pure samples investigated by Hébert melted at 36 to 37° but not sharply, the fatty acids belonging thereto (51 to 70 per cent.) at 39°, the ash content varied between 0.6 and 1.2 per cent. According to Hébert and Charabot the saponification value of civet must be higher than 100.

We may now allow our own observations to succeed the foregoing. We will first say, that with several samples of civet obtained from trustworthy sources, we have found an ash content of 1.09 to 2.15 per cent., an acid value of 47 to 89, an ester value of 23 to 75, and a sap. value of 70 to 128, *i. e.*, values which vary greatly, and with which alone there is little to start with. Also, in our opinion, the behaviour of the civet in a mixture of alcohol and ether often gives no information of its condition, whilst the successive extraction with acetone and light petroleum promises more success in this respect. Hence we have followed this latter method, only we use other solvents than acetone and petrol ether, *viz.*, alcohol, ether and chloroform when they seem more advantageous for the purpose at hand. The chloroform is used to dissolve the resin products insoluble in alcohol, and also in ether. In order to save time and avoid triturating the civet with a diluting material, such as sand, and the like, we do not perform the extraction in a Soxhlet apparatus, but simply shake up the civet with the necessary solvent, and then continue the extraction with the same solvent on the filter. This causes less bother and, apart from the saving in time, possesses the advantage of allowing one to further examine the insoluble portions. We proceed as follows:—

5 g. civet are melted in an acetylating flask on the water bath, and are shaken up hot, at first with about 20 cc., and then three times, each time with the addition

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[1]) *Bull. Soc. chim.* III, 27 (1902), 997. *Bericht* (German edition) April 1903, 104. — [2]) *Chemist and Druggist* 61 (1902), 901; 62 (1903), 871; 65 (1904), 168. *Bericht* (German edition) April 1903, 104; October 1903, 109; October 1904, 143. — [3]) *Analyst* 28 (1903), 101. *Bericht* (German edition) October 1903, 110. — [4]) *Bull. Soc. chim.* IV. 7 (1910), 687. *Report* October 1910, 150.

of 15 cc. 90 per cent. alcohol, which with a little foresight, will avoid the spitting of the civet into the vertical tube. After each cooling—hastened by dipping in water—the extract is filtered through a weighed quantitative filter paper, and finally again washed several times with alcohol, until the filtrate amounts to 100 cc. The residue remaining partly in the flask, and partly on the filter paper, is at once treated repeatedly, at room temperature, with ether (altogether about 60 cc. filtrate). The whole of the residue can now be transferred to filter paper with ease, and washed with chloroform, pouring it on carefully at the start with the aid of a stirring rod (about 30 cc. filtrate).

Each filtrate in its own saponification flask is placed on the water bath and the solvent distilled, and the flasks are then placed in the vacuum dessiccator to get rid of the last traces of solvent. With the alcoholic extract, and sometimes also with the ether extract, it is necessary after distilling off solvent, to let the flask stay for some time longer on the water bath, and draw air through, rotating flask as often as possible, and taking care that the glass tube dipping deeply into the flask does not touch the civet extract. The flasks are placed in a lying position in vacuum dessiccator, for otherwise, on evacuating a loss can happen by spirting, as the water vapour, accompanied by bubble formation, escapes. Finally the weight, acid value, and ester value of each extract is determined.

By weighing the filter after drying at 100° the part of the civet insoluble in the solvent used can be found, and from the difference between quantity of civet used and extracts + residue, the water content. If necessary, the ash content can be found by ignition of filter, and the ash further examined.

With a little practice, this method can be carried out quickly and smoothly. We have carried out this method of investigation for a series of years and are quite satisfied with it:—If the material for investigation has not yet reached the desired quantity in spite of the length of time, it is due to the fact that scarcely any civet arrived during the war years, and that even now, a pure sample is a rarity, at least in our experience, as we shall show later by a few examples. With 12 civet samples, coming from very trustworthy sources, and which could claim to be pure and good, according to their whole behaviour, we have obtained the following results by using the above method:—

	Per cent.	Acid value.	Ester value.	Sap. value.
Alcohol extract . .	45.8 to 58	118.2 to 147.3	29.0 to 53.0	155.4 to 182.8
Ether extract . . .	12.6 „ 19.9	7.9 „ 18.0	64.9 „ 89.7	75.9 „ 96.9
Chloroform extract .	0.3 „ 6.4	5.9 „ 20.0	78.0 „ 155.0	98.0 „ 160.9
Residue	5.4 „ 9.5	—	—	—
Water	13.5 „ 21	—	—	—

As is seen, these values also are subject to great variations, yet as a whole, they give a very good idea of the quality of the civet, and very well permit of a qualitative judgment. On account of the comparative scarcity of material it is apparent that these values can make no claim to unconditional validity, and only time will show in how far they are correct. Yet even at present they can be of use to the analyst. The figures need no explanation, yet it should be again repeated that the amounts of residue observed by us do not agree with those given by Hébert and Parry; for on the one hand we have never found so low a quantity as 3 per cent., and have repeatedly found over 6 per cent., and as, as already mentioned, we went very carefully to work in determining the limiting values, we have no reason, on account of these differences, to doubt the goodness of the civet samples used by us as basis.

It is still desirable, for purposes of examination, to know the melting points of the various extracts, and we will later on extend the investigation in this direction.

We mentioned above that we have had no satisfactory experiences lately with the civet on the market, and of the examined samples will only mention those, which show in a specially remarkable manner, the unheard-of methods employed by some in adulteration, and to show the necessity of a thorough examination even for this article. A well-known Parisian firm sent us one sample of civet described as *garantie pure*, whilst the other two offered us for sale came from Cologne and London respectively. It turned out that the Parisian and Cologne goods contained considerable quantities of vaseline, whilst about half of the London sample consisted of talc. These additions naturally had a very strong influence of the result of the analysis, as a comparison of the following summary with the above limiting values will show.

	Per cent.	Acid value.	Ester value.	Sap. value.
		I. Paris		
Alcohol extract	35.2	116.7	20.0	136.7
Ether extract	48.1	11.1	36.3	47.4
Chloroform extract	4.5	7.5	124.5	132.0
Residue	3.8	—	—	—
Water	8.4	—	—	—
		II. Cologne		
Alcohol extract	43.3	100.9	17.6	118.5
Ether extract	44.0	5.9	37.4	43.3
Chloroform extract	2.8	12.0	152.0	164.0
Residue	4.4	—	—	—
Water	5.5	—	—	—
		III. London		
Alcohol extract	29.5	121.4	34.5	155.9
Ether extract	7.1	8.0	102.8	110.8
Chloroform extract	—	—	—	—
Residue	52.6	—	—	—
Water	10.8	—	—	—

The ether extract was considerably raised by the vaseline (civet I and II), whilst on the other hand their ester value and sap. value were lowered. The lowerings of the acid value, ester value and sap. value of the alcoholic extract is also noteworthy, which shows that a small quantity of vaseline is also taken up even on extracting with alcohol. Apparently more vaseline has gone into solution in the case of II than in I, from which it is explainable that in I the alcohol extract is greater and its acid value, ester value and sap. value smaller than in I. The addition of vaseline has, moreover, lowered the residue and the water content of both. From the quantities of the ether extracts one can assume that the vaseline content of I amounted to at least 30 per cent., and of II to at least 25 per cent. The vaseline was also recognisable by the blue fluorescence of the solution.

The admixture of talc in III showed its presence in a different way. The first thing that strikes one is the tremendous increase in the residue, which goes hand in hand with a lowering of the alcohol- and ether-extract, as well as that of the water content. The incineration of the residue showed that it was mostly inorganic and consisted almost wholly of talc, the amount of which came to over 45 per cent. of the original civet. The normal saponification constants of ether- and alcohol-extracts

lead to the conclusion that no further adulteration had taken place. Quite enough had already been done!

From the foregoing it is seen that the examination of civet is still a bit of a bother, and will prevent many from undertaking it. This naturally encourages adulteration, and for many therefore, civet is a safe article; consequently it should only be obtained from trustworthy importing firms.

Cumarin. — *Re* volatility of cumarin see p. 77 of this *Report*.

Heliotropin. — *Re* volatility of heliotropin see p. 77 of this *Report*.

Jonone. — Supplying the perfume trade with violet perfumes was greatly hindered by the difficulties met with in procuring the raw material, especially of obtaining sufficient quantities of lemongrass oil; so that the lively demand at home and abroad could not always be met. On account of the expected arrival of greater quantities of lemongrass oil within the next few months, an improvement in the delivery possibilities is to be looked for with certainty.

Menthol. — As an effective remedy for lice and flies, menthol (1 to 3 per cent.) mixed with zinc oxide is recommended[1]).

Menthylvalerianate. — *Re* saponification of menthylvalerianate see p. 94 of this *Report*.

Musk. — We already reported on the musk industry in the *Report* 1918, p. 64. The following details taken from the "North China Daily News"[2]) may serve as a supplement.

From Tachienlu, Szetchuan, about 30000 musk pouches valued at 300000 taels are dispatched annually. Since about 60000 musk animals are killed annually by the Chinese and the Thibetans, it is to be feared that with the growing demand, they will in time become extinct. The Chinese and Thibetans catch the shy musk deer, which live in seclusion in the wooded highlands, in their feeding and drinking places with traps and slings the whole year through; the best goods however, are obtained in autumn and winter. In Tachienlu the musk-sacs are steeped in water, freed from skin and hair, and packed carefully in small wooden boxes for export.

In order to test the quality of musk, which is often adulterated with peas, barley, crushed acorns, roasted liver or powdered beef, the Chinese merchants use three instruments:—

(1) A thick, blunt 4 in. long needle, with which the natural opening of the sac can be enlarged without damage.
(2) A hooked needle, for extracting from the sac for examination any hidden hard substance that may be there.
(3) A curved hollow needle, for withdrawing a small amount of musk for examination.

According to an American source[3]), the export of musk from China in normal years amounts to over $ 375000. The World War, together with the internal unrest resulting from it, has greatly diminished the musk trade. The drug is chiefly obtained in the Thibet-Chinese border lands, and the town of Tachienlu with a turnover of about

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[1]) *Journ. Trop. Med. and Hyg.* 18 (1915), 254; As per *Digest of Comments on the Pharmacopœia of U. S. A. for* 1915, 315. — [2]) From *Pharmaceutical Journ.* 103 (1919), 285. — [3]) *Drug and Chemical Markets* VI. 6.

300000 taels, occupies the premier position in the trade. The musk pouches are brought there to the market from the far interior by hunters, and traders. A sac contains from 1 to 2 ounces of pure musk. The musk is forwarded to the coast during the cold season of the year, for heat and moisture lower the quality. Only about 80 per cent. of the exported musk can be regarded as pure, since adulterations with peas, wheat and barley-corns, ground acorns, roasted liver and pulverised beef, are the order of the day, on account of the high value of the commodity.

In recent years the prices of musk in Tachienlu amounted to:—

1914 . . .	15 taels per ounce	1917 . . .	11 to 12 taels per ounce
1915 . . .	13 „ „ „	1918 . . .	11 „ 12 „ „ „
1916 . . .	11 „ „ „	1919 . . .	12 „ 14 „ „ „ .

The value of the Haikwan tael, which serves as basis for reckoning has risen from $ —.65 in 1914 to $ 1.20 at end of 1919.

On account of high prices and unsatisfactory currency conditions, only very modest quantities of genuine musk were imported into Germany during the War.

Nitrobenzene. — One is continually reading of cases of nitrobenzene poisoning. Hence it should again he pointed out how dangerous this preparation is, even when diluted. Tuscevski[1]) writes about three cases, in which after partaking of oil of mirbane cyanosis, coma, convulsions, and injury to the spinal cord supervened. One patient died. On another occasion soldiers received the oil preparation instead of fennel oil, as a remedy against body lice. After rubbing it into their bodies, six of them fell sick with symptoms of severe poisoning; one case was hopeless[2]). K. Bohland relates the case of a girl who purchased at the druggists as "Vermin-spirit", sabadilla vinegar, with an underlying layer of nitrobenzene. It had to be shaken before using. When she had rubbed it into the scalp three times, very serious poisoning symptoms appeared[2]). Another severer case of poisoning was, according to Wandel[3]), probably caused by spirits containing nitrobenzene, and Heller[2]) established the fact, that almond-flavoured essences chiefly contained nitrobenzene. He demands that the unchecked sale of nitrobenzene should cease, and that its use should be strictly supervised by the authorities[4]).

Oregon Balsam. — According to information from people conversant with the winning of this balsam, the resin is obtained in two ways from the Douglas pines (*Pseudotsuga taxifolia*, Britton; *P. Douglasii*, Carr.). (1) The trees are felled; the balsam which then flows out is received in suitable vessels. (2) The trees, in which cavities have occurred caused by a squall, and gradually filling themselves with the resin, are bored by experienced collectors. With help of a tube the out-flowing balsam (1 to 3 gallons are frequently obtained from a single boring) is collected in pails[5]).

In view of the doubtless need for improvement in this method of winning, S. A. Mahood[6]) proposes the application of the European methods of getting larch turpentine, where one or two holes 1 to 1½ inches wide are bored in the spring, in an almost vertical direction in the fully grown trees (of about 40 ft. girth) right into the middle of the trunk. The trees without cavities should also be bored. The bore-holes are

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[1]) *Münch. med. Wochenschr.* **44** (1919). As per *Pharm. Ztg.* **64** (1919), 845. — [2]) *Deutsche Med. Wochenschr.* **45** (1919), 1388. As per *Deutsche Parf. Ztg.* **6** (1920), 6. — [3]) *Therap. der Gegenwart* **1919**, 226. As per *Therap. Halbmonatsh.* **34** (1920), 60. — [4]) Cf. *Report* **1918**, 5. — [5]) See also *Report* **1918**, 36. — [6]) *Americ. Journ. Pharm.* **91** (1919), 345.

plugged, till after a given time, the collecting balsam is allowed to drip out. Freshly felled trees can also often be tapped with profit. The trees are said to suffer little from the boring, and often yield balsam through the same bore-holes for 20 to 50 years.

The demand for Oregon balsam appears to increase. The market price has risen and amounts to $ 1.75 to 1.80 per gallon (1. Feb. 1919).

The balsam is used in place of Venetian turpentine for the preparation of varnish, porous plasters, and in the ceramic industry. The name "balsam" is false in both cases, for not balsams, but turpentines are present.

The acid value of the non-volatile residue of Oregon balsam amounting to 70 per cent., is 153 according to Rabak, and 166 according to Schorger. The balsam is no artificial product (solution of colophony in oil of turpentines), as Dowzard had assumed by reason of the high acid value, which was almost identical with that of colophony (155). Oregon balsam and Canada balsam appear to be distinguishable by the acid values. Indeed the important constituents of these two vegetable secretions are quite similar, and in many cases Oregon balsam, which is six times cheaper than Canada balsam, can be used for the same purpose.

Peru Balsam. — The estimation of the iodine number of cinnamein (Oil of Peru Balsam) by the method of Hanus is said by E. C. Merrill[1]) to be untrustworthy. The author has proved that the usual duration of 30 mins., employed for the reaction is too short, and ought at least to continue for three hours. There is no difference in viscosity between genuine and artificial balsam. According to Merrill, the cinnamein of artificial balsam has a slight optical rotation α ($[\alpha]$?) $= +0.35°$ (20 vols. per cent. cinnamein solution in benzene), $n_{D25°} < 1.57$; the cinnamein of the genuine balsam is on the contrary, optically inactive, $n_{D25°} > 1.57$.

What Merrill says about the optical behaviour of the cinnamein separated from natural balsam, does not agree with our experience, for we have always found a slight rotation to the right up to $+2° 30'$. Since our investigations extend over decades, therefore we then would never have had in this long period a genuine balsam in our hands, which indeed Merrill will not believe. His statement therefore must be correspondingly altered[2]), unless indeed there is an error in the abstract.

Phenylethylalcohol. — A phenylethylalcohol of French origin, which came to our laboratory for examination, and was extolled as especially good, may serve as an example with what sort of a preparation one will defy all competition. The following are its constants placed side by side with those of pure phenylethylalcohol:—

	Sample	Pure Phenylethylalcohol
$d_{15°}$	0.9969	1.023 to 1.027
α_D	$\pm 0°$	$\pm 0°$
$n_{D20°}$	1.51799	1.530 to 1.535
Solubility in 50 per cent. alcohol	sol. in 4 vol. and more, from 6 vol. on cloudiness	sol. in 2 vol. and more

A comparison shows distinctly that it was no pure product, for the sample differs so greatly from the normal that it could not be recognized as phenylethylalcohol by its constants. The same may be said of its smell, which was absolutely different from that of phenylethylalcohol and reminded one rather of oil of rue or coconut oil.

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[1]) *Journ. Assoc. Off. Agric. Chem.* **3** (1919), 194. As per *Journ. Soc. Chem. Ind.* **39** (1920), A. 348. — [2]) Cf. also the investigations of Rosenthaler, *Report* April **1915**, 57, also those of Sortell, *ibidem* 58.

Since this discovery rendered it completely uncertain whether phenylethylalcohol was really present at all, we directed our further investigations in this direction. It turned out that the preparation contained about 60 per cent. of phenylethylalcohol, whilst the remainder was made up of compounds, probably some waste product or other, which could be only designated as worthless ballast.

The buyer of these kinds of "valuable" products generally finds out too late that he has been scandalously overcharged.

Pollantin.—The pollen of the ambrosia species amongst others, especially of *Ambrosia trifida*, L. and *A. artemisifolia*, L. belong to the exciters of American fall fever, which in its symptoms resembles hay fever. The labours of F. W. Heyl[1])—which in the meanwhile have been carried on[2])—have proved that besides toxic albumin, also other well defined chemical bodies are found in the pollen of these composites, which are found also here and there in Germany.

The constituents of the pollen which cause the yellow colour are glucosides closely related to flavone. To obtain them Heyl extracted the ether-extract of the pollen with alcohol, dissolved the alcoholic extract in water, precipitated with lead subacetate, and decomposed the precipitate with hydrogen sulphide. In this manner he obtained from 1150 g. pollen 7.0 g. *i. e.* about 0.6 per cent., of a yellow substance, from which he was able to isolate two glucosides.

The part of the precipitate less soluble in water contained a glucoside of the composition $C_{21}H_{20}O_{12}$, which could be split up into glucose and quercetin $C_{15}H_{10}O_7$, and which was isomeric with the glucosides quercimeritrin and *iso*quercitrin isolated from the flowers of *Gossypium herbaceum*, Linn. by A. G. Perkin[3]). An absolute characteristic of this ragweed glucoside is, that the substance, which crystallizes in bright yellow needles, changes suddenly on melting (m. p. 228 to 229°) to a cherry red oil.

The second glucoside of the pollen was obtained in splendid hexagonal crystals extremely soluble in water. On hydrolysis it yielded *iso*rhamnetin (m. p. 197 to 200°), the quercetin-3-methylester, which had been found also in the flowers of *Cheiranthus Cheiri*, L.[4]) and *Trifolium pratense*, L.[5]).

Storax.—P. Bohrisch[6]) has published an exhaustive treatise on the investigation of purified storax. The author investigated four samples, 2 of which were adulterated and the other two in all probability identical, and sums up the results of his labours as follows:—(1) The colour of purified storax should be strongly brown. If yellow-brown or yellow, adulteration may be suspected. (2) The smell of pure storax reminds one of benzoin. Storax with an odour of cinnamon oil has been perfumed, and is probably an artificial product. (3) The specific gravity of purified storax can be approximately determined in a graduated cylinder. (4) The qualitative test of the German Pharmacopœia often fails. If the filtrate is evaporated to dryness and the residue warmed with a few drops of dilute sulphuric acid and 5 cc. of permanganate solution, then, if cinnamic acid is present, the smell of oil of bitter almonds appears. (5) The determination of acid value and saponification value frequently furnish no decisive point for an adulteration of storax, since the limiting numbers allow too much room for play, and are not absolutely established. Hence it is advisable to resort to further methods of investigation of suspicious storax. The estimation of the light petroleum extract, as

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[1]) Cf. *Report* 1918, 65. — [2]) *Journ. Americ. chem. Soc.* 41 (1919), 1285. — [3]) *Journ. chem. Soc.* 95 (1909), 2181. — [4]) *Ibidem* 69 (1896), 1658. — [5]) *Ibidem* 97 (1900), 245. — [6]) *Pharm. Zentralh.* 61 (1920), 275.

well as its acid value and saponification value is useful, if it is a case of adulteration with colophony. On the contrary it is of little value with other adulterants. In this case the estimation of the cinnamic acid is of value. It is best carried out according to the process of Hill and Cocking[1]). (6) A cinnamic acid content of 21 to 30 per cent. was found for genuinely pure storax by their methods. It appears doubtful whether these numbers are decisive for the judging of pure storax. (7) At present a so-called purified storax is found — apparently very frequently — in German trade which is an artificial product treated with cinnamon oil, but containing no cinnamic acid.

In the two genuine samples Bohrisch found 4.3 and 5.1 per cent. cinnamic acid; and in another sample obtained from K. Dieterich of guaranteed genuine, raw storax, he found 12 per cent. cinnamic acid. A satisfactory explanation of the small cinnamic acid content could not be found. K. Dieterich assumes that in the evidently old samples a transformation of the cinnamic acid had occurred.

Tsuchihashi and Tasaki[2]) have investigated two different sorts of storax from *Liquidambar formosana*, Hance, one of which (a), was solid, and the other (b) was semi-solid and viscous. The balsams had the following properties:—

	a	b
Volatile substances	1.4 per cent.	4.6 per cent.
Constituents volatile in steam	1.8 „ „	8.0 „ „
Ash	0.9 „ „	0.1 „ „
Constituents soluble in ether alcohol	93.4 „ „	82.7 „ „
Constituents insoluble in ether alcohol	5.7 „ „	17.2 „ „
Acid value	43.5	34.2
Saponification value	95.4	101.5

From balsam (a), which contained no cinnamic acid, a resin alcohol of melting point 155 to 161°, $[\alpha]_D + 53°$, was isolated, which is probably identical with the "Styresinol" $C_{16}H_{26}O_2$ of Tschirch. In balsam (b) besides 16 per cent. of cinnamic acid, cinnamic alcohol and borneol were also found.

Thymol. — The supply to the pharmaceutical industry of this important substance since the end of the war just sufficed. Whilst in 1914, when Germany was yet producing the largest quantities, it could be purchased at about Mk. 10 per kilo; the small imports mostly from England and Spain of very doubtful quality cost now about Mk. 1000 per kilo. Only a little came on the European market from U. S. A., where its preparation said to have been taken up on a large scale. The Spanish product is obtained from is oil of thyme, and consequently its price is dependent on the market value of the latter, and which indeed has risen considerably in price recently.

According to an American patent (U. S. Pat. 1306512)[3]) thymol is obtained by nitrating aminocymene, whose amino group is protected. By removing the amino group nitrocymene is obtained, and then thymol, by substituting hydroxyl for the nitro group.

As an antiseptic thymol is similar in many respects to phenol, and cresol; as however it is only slightly soluble in water, it would probably be less easily absorbed by the alimentary canal[4]).

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[1]) Cf. *Report* October 1912, 125. — [2]) *Chem. Umschau* 26 (1919), 226. As per *Pharm. Zentralh.* 61 (1920), 275. — [3]) *Journ. Soc. chem. Industry* 38 (1919), A. 658. — [4]) *Journ. Americ. Med. Ass.* 66 (1916), 746. As per *Digest of Comments on the Pharmacopœia of the U. S. A. for* 1916, 296.

Schultz[1]) studied the influence of various solvents on the effectiveness of thymol, and found that, when dissolved in oil it lost the greater part of its antiparisitic qualities.

Vanillin. — We met with a gross case of adulteration in a sample sent to us for examination. It contained 20 to 30 per cent. of a substance apparently consisting of wheat groats. Such an admixture betrays itself very quickly by reason of its insolubility in ether, and alcohol; it would also be quickly observed by the consumer, since he often uses it in alcoholic solution. Unfortunately the amount of sample at our disposal was so small, that we could only approximately decide the amount of admixture. On treatment with ether, a residue of 20 to 30 per cent. remained, which on viewing with the naked eye and also under the microscope, was quite apparently identical with wheat groats. The vanillin reobtained from the solution in ether melted at 82°, and was hence of usual quality.

H. Sprinkmeyer and O. Grünert[2]) made investigations on the identification, and especially on the volatility of vanillin, cumarin, and heliotropin in mixtures, as in the so-called aroma powders; which led to the following results: —

(1) The amount of vanillin, cumarin and heliotropin in mixtures gradually decreases on keeping. (2) Of these three aromatic substances, heliotropin is the most unstable. (3) Within the space of 3 months a loss of up to about 81 per cent. of the aromatic substance was observed in the case of vanillin and cumarin. If the vanillin is partly replaced by heliotropin in the mixture, then the disappearance of aroma is greatly increased; by the end of a month the whole of the heliotropin had disappeared, and only a part of the vanillin was still present. (4) In mixtures where vanillin only is used, the less the quantity of vanillin, the more rapidly does it decrease. (5) The disappearance of the aromatic substance is more rapid in flour than in sugar-mixtures. (6) Colour reactions are insufficient for determining the purity of vanillin; the most valuable test is the melting-point.

In reference to these investigations of Sprinkmeyer and Grünert, H. Schellbach and Fr. Bodinus[3]) report that they found only an 8 to 10 per cent. disappearance of vanillin in 45 samples of commercial 1 per cent. vanillin sugar from 3 to 6 months after their preparation. The volatilisation of vanillin ascertained by Sprinkmeyer and Grünert was much greater in considerably lesser time. The colour reaction for vanillin and heliotropin first established by Schellbach and Bodinus[4]) is useful when pure substances are present. If a red coloration appears with resorcinol + hydrochloric acid, but no blue coloration with ferric ohloride, then heliotropin alone, or heliotropin and cumarin are present.

Supplementary to their first announcement on vanillin preparations (see above), H. Sprinkmeyer and O. Grünert[5]) published further results of their investigations in this matter. They were able to confirm their earlier investigations and also show that the disappearance of the aromatic substance in vanilla sugar could be very greatly retarded if packed in parchment bags or small glass tubes instead of ordinary writing paper. The disagreement of their observations with those of Schellbach and Bodinus (see above) may be found due to the different ways in which the article was packed.

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[1]) *Chem. Abstr.* **10** (1916), 2598. As per *Digest of Comments on the Pharmacopœia of U. S. A. for* **1916**, 296. — [2]) *Zeitschr. Unters. d. Nahrungs- u. Genussm.* **38** (1919), 153. — [3]) *Ibidem* 292. — [4]) *Ibidem* **36** (1918), 187. Vanillin and heliotropin both give with resorcinol + sulphuric acid, and with resorcinol + hydrochloric acid (d 1,19) an intense splendid red coloration. Cumarin does not give this reaction. — [5]) *Zeitschr. Unters. d. Nahrungs- u. Genussm.* **39** (1920), 145.

The result of the vanilla crop for season 1919 to 20 was as follows[1]):—

On Madagascar and the islands belonging thereto	Comoro Island	403204 lbs.
	East Coast	423503 „
	Nossi Bé	110230 „
	Total:	936937 lbs.
On Mauritius		2646 „
„ Réunion		198414 „
„ Seychelles		6614 „

[1]) *Commerce Reports*, 19th March 1920. As per *Americ. Journ. Pharm.* 92 (1920), 356.

Notes on Scientific Research in the Domain of the Terpenes and Essential Oils.

General.

F. B. Power[1]) has published a paper on the *occurrence,* the *winning* and the chemical *composition* of *plant perfumes,* which in a condensed form gives an interesting and instructive view over the domain of the essential oils. The multiplicity of the substances which condition the odour is great. Every plant family, almost every species has its own characteristic odour; indeed, even the various parts of one and the same plant may form quite various odorous substances. The oil got from the roots of the sassafras tree *Sassafras variifolium,* Kuntze (similar to *S. officinale,* Nees) contains safrole, camphor, eugenol, &c., *i. e.,* substances which are not present in the leaves; on the other hand myrcene, citral, linalool and geraniol are found in the leaves only of this plant. We have a similarly known example in the Ceylon cinnamon tree *Cinnamomum ceylanicum,* Nees, whose roots contain camphor, whose leaves chiefly contain eugenol, whilst in the bark oil cinnamic aldehyde prevails.

Environment, difference in the soil and climate have great influence on the composition of plant perfumes of otherwise similar origin. Thus in oil of thyme, instead of the generally occurring thymol (*iso*propyl-*m*-cresol), the isomeric, fluid carvacrol (*iso*propyl-*o*-cresol)[2]) is occasionally found. Oil of lavender, that is distilled in France from the wild growing *Lavandula vera,* DC., is characterised by its amount of pleasant-smelling linalool $C_{10}H_{18}O$ and its ester, together with geraniol, whilst the oil got from the cultivated English plant contains much less ester and a comparatively large quantity of the camphor-like smelling cineole $C_{10}H_{18}O$.

A single substance seldom conditions the characteristic odour of plants; generally a mixture of substances is present, amongst which, perhaps, one prevails.

These odorous substances — called essential or volatile oils — are generally obtained by steam-distillation. In cases, where the oil first originates through the splitting up of a glucoside, as in mustard seed, bitter almonds, gaultheria leaves and birch bark, the drug must be first digested in water for some time before being distilled. A few essential oils, whose aroma might be lessened by being distilled, particularly those the "Agrumen fruits", orange (sweet and bitter), lemon, and bergamot are obtained by pressure. In other cases the scent of certain flowers is of so delicate a nature that it is only obtainable in fair quantities when extracted with a volatile solvent, or macerated with oil or fat. The use of heat in such macerations appears advantageous for obtaining the odorous substances from violet, orange, and cassie flowers. Together with this method of extraction, named *enfleurage à chaud,* a process of cold maceration — *enfleurage à froid* — is used for other blossoms, such as jasmine, tuberose, jonquille, lily of the valley, and mignonette. The odorous substances in the plants named in the last process, are only present in very small amounts, but are being continually produced by the

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[1]) *Journ. ind. eng. Chem.* **11** (1919), 344. According to kindly forwarded special print. — [2]) Cf. also oil of *Mosla japonica;* this *Report* p. 40.

living cells during the *enfleurage*. Since volatile solvents or warm fat destroy the life of the cells, the blossoms are spread on cold fat, which continually absorbs the perfume that is being generated. For *enfleurage* so-called "châssis" are used — wooden frames 5 cm. high and from 50 to 80 cm. square — which carry glass plates in the middle, spread on both sides with a specially prepared fat. The blossoms (without calyx) are spread on one of these fat-layers, and then 35 to 40 such "châssis" are piled on the top of each other. Thus the blossoms are enclosed in a sort of chamber, each layer of blossoms lying between two layers of fat. After from 24 to 72 hours the used blossoms are replaced by fresh. When the fat has taken up sufficient perfume-substance, it is extracted with strong alcohol. From the *extrait aux fleurs* thus obtained, the much-prized plant perfumes *(essences)* are won.

After this general introduction, Power discusses in detail the individual perfume substances of the various plants, in so far as they are of importance, or have a special interest for the perfume industry.

Of the oils of the conifers, turpentine oil may be mentioned as raw product for the preparation of terpineol. Whilst this artificial preparation is a mixture of isomeric α- and β-terpineol, terpineol is found in nature only in the active or inactive α-form. The dextro modification occurs in cardamom, linaloe, neroli, lovage and sweet-orange oils; the lævo form is present in camphor oil, linaloe oil, and in Canadian snake-root oil; inactive terpineol is got in the solid condition from cajuput oil, and in liquid form from nutmeg oil and boldo leaf oil.

The essential oils obtained by the distillation of pine needles differ considerably from the turpentine oils obtained from the resins, since in the former pinene is replaced in great measure by other terpenes, such as camphene, limonene or dipentene, phellandrene, sylvestrene and cadinene. They also contain considerable quantities of bornyl acetate (the needle oil of the hemlock pine *Abies canadensis,* Michx., contains about 50 per cent.), an ester having the characteristic pine odour and used in perfumery. Of special interest is the essential oil obtained from the nut pines, *Pinus Sabiniana,* Douglas, and *Pinus Jeffreyi,* Murray, growing on the western slopes of the Sierra Nevada, since it has the lowest specific gravity of all known essential oils, and consists almost entirely of heptane, a constituent of petroleum. The cedar wood oil of *Juniperus virginiana,* L., used in the soap industry is remarkable on account of its cedrene ($C_{15}H_{24}$) content — a sesquiterpene, and its cedrenol content ($C_{15}H_{24}O$) — a sesquiterpene alcohol.

The gramineæ family yield a number of essential oils, as palmarosa, gingergrass, lemongrass, vetiver oils, which are of great importance in trade and industry. In year 1902/03 123000 lbs. palmarosa oil were exported[1]) from India; the yearly amount exported from Bombay alone is reckoned to be 50000 lbs.

Whilst palmarosa oil with its pleasant odour of roses contains chiefly the aliphatic terpene alcohol geraniol, $C_{10}H_{18}O$, the aldehyde citral, $C_{10}H_{16}O$, corresponding to geraniol forms the chief constituent of the lemon-smelling lemongrass oil. Apart from its dissemination in nature, citral is of great technical importance, as *pseudo*-ionone is obtained from it by condensation with acetone, and also the isomeric cyclic ketone ionone, the chief ingredient of artificial violet perfumes.

Among the trees of the palm family few perfume substances are obtained. It is interesting to know however that on treating crude coconut oil with steam under pressure, an unpleasant smelling essential oil has been obtained. Methylheptylketone, $CH_3COC_7H_{15}$, and methylnonylketone, $CH_3COC_9H_{19}$, in addition to the corresponding

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[1]) Cf. also *Report* **1917**, 32.

carbinols $CH_3CH(OH)C_7H_{15}$ and $CH_3CH(OH)C_9H_{19}$ were found in this oil; compounds which we know as constituents of oil of rue. But whilst the alcohols from coconut oil are dextro-rotatory, those got from the oil of rue are lævo-rotatory. Palm kernel oil treated in the same way yields an essential oil with up to 90 per cent. methylnonylketone[1]).

The family of the *Liliaceæ* is noteworthy on account of a few onion species, as garlic, *Allium sativum*, L., and the common onion, *Allium Cepa*, L., whose essential oil contains sulphur compounds and emits an unpleasant smell. The chief constituent of these plants is not allyl sulphide $(C_3H_5)_2S$, as was for long enough assumed, but a mixture of more complex sulphur compounds. In the same family we also find pleasant smelling plants as the hyacinth, *Hyacinthus orientalis*, L., and the lily of the valley, *Convallaria majalis*, L., whose odoriferous principles have not yet been thoroughly investigated. Yet it is known that the hyacinth contains benzyl benzoate, free benzyl alcohol and also esters of cinnamic alcohol. These perfumes have been very successfully imitated in various ways; thus phenyl acetaldehyde $C_6H_5CH_2CHO$ has a strong smell of hyacinths and is consequently greatly used in perfumery. The smell of the lily of the valley comes in great part from the aliphatic sesquiterpene alcohol farnesol, $C_{15}H_{26}O$, contained also in cassie blossoms (*Acacia Farnesiana*, Willd.), in the blossoms of the common acacia (*Robinia Pseudacacia*, L.), in lime flowers (*Tilia europaea*, L.), elder flowers (Spanish lily) (*Syringa vulgaris*, L.) and in mignonette (*Reseda odorata*, L.).

Amongst iris species, as *Iris germanica*, L., *I. pallida*, Lamb., and *I. florentina*, L., family of the *Iridaceæ*. we find that the rhizome has a decided smell of violets especially after drying This odour originates from quite a small quantity of an essential oil (0.1 to 0.2 per cent.), which is solid at ordinary temperature, and contains up to 85 per cent. of the quite odourless myristic acid. The constituent which occasions the characteristic violet odour is the fluid cyclic ketone irone $C_{13}H_{20}O$. In isolating and examining this body, the isomeric ketone ionone was successfully synthesised; this ketone has already been mentioned.

A very fine perfume substance used in the preparation of favourite perfumes is contained in the blossoms of *Cananga odorata*, Hooker f. et Thomson, an anonacea disseminated in East Asia. In Manila the tree is known by the name "ylang-ylang". In most of the provinces of the Philippines on the contrary, it is called "alangilang". The word describes the loosely hanging blossoms and twigs fluttering in the wind. The composition of the oil is very complex, and is not yet thoroughly known. Yet it is known that *l*-linalool and geraniol as esters of benzoic acid, further methyl benzoate and salicylate, benzyl acetate and benzoate and free benzyl alcohol are present in the oil. In addition, the methyl ether of *p*-cresol, formic acid, safrole and the terpenes *d*-α-pinene, cadinene and a little methyl anthranilate have been found therein.

The family of the *Myristicaceæ* yield the universally known spices nutmeg and mace. More than 20 substances have been identified in the oils therein contained. Myristicin, $C_{11}H_{12}O_3$, the constituent of highest boiling point is 3-methoxy-4,5-methylenedioxy-1-allyl benzene and causes the narcotic effect of nutmeg, which has been observed in cases of so-called nutmeg poisoning. The base cotarnine or stypticine $C_{12}H_{15}O_4N$ is obtained from myristicin by a series of reactions; it is an oxidation product of the opium alkaloid narcotine $C_{22}H_{23}O_7N$.

Amongst the *Lauraceæ* we find a series of plants, whose products are of not only great interest for the chemist, but also possess considerable commercial importance. Besides camphor, used in large quantities in the preparation of celluloid, smokeless powder and for medicinal purposes, camphor oil should be mentioned — the by-product of

[1]) Cf. *Report* 1918, 38.

the Japanese camphor industry. From the 25 bodies, which can be actually identified in camphor oil, amongst other things, safrole $C_{10}H_{10}O_2$, can be obtained, the chief constituent of oil of sassafras. Safrole is used as a scent for soaps, and when transformed into *iso*safrole it is used for the preparation of piperonal or heliotropin. It is also remarkable that camphor oil contains the same constituents as oil of sassafras, and that in carefully fractionating, a product can be got from camphor oil which can scarcely be distinguished from sassafras oil. It comes on the market under the wrong and deceptive name "artificial sassafras oil". The leaves of the American bay tree, *Umbellularia californica*, Nutt., yield 2 to 5 per cent. of an essential oil smelling like camphor. If strongly inhaled, the oil attacks the mucous membranes of the nostrils and eyes. These properties are ascribable to a ketone umbellulone, $C_{10}H_{14}O$. If umbellulone is heated to 280° for several hours in a closed tube, it is transformed quantitively by intramolecular change into thymol.

Several products found in the *Cruciferæ* are known by the name of mustard oils. These oils, generally engendered by the reaction of an enzyme on a glucoside, consist chiefly of esters of *iso*thiocyanic acid HN·CS. We may call to mind here the volatile oil obtained from the seeds of black mustard, *Brassica nigra*, Koch, and *Brassica juncea*, Hooker f. et Thomson, consisting almost entirely of allyl*iso*thiocyanate $CH_2:CH\cdot CH_2NCS$, and which is synthesised in large quantities by the reaction of allyl iodide on potassium thiocyanate in alcoholic solution. The essential oil got from the common horse-radish root, *Cochlearia Armoracia*, L., has a composition quite similar to that of usual mustard oil. The "colza seeds", *Brassica Napus*, L., on the contrary, contains a volatile oil that consists of crotonyl*iso*thiocyanate, $CH_2:CH\cdot CH_2\cdot CH_2NCS$. It may not be generally known that on steam-distilling the fresh roots of garden mignonette, *Reseda odorata*, L., a mustard oil of a radish-like odour is obtained that chiefly consists of phenylethyl*iso*thiocyanate.

We thank the *Rosaceæ* family for two important products, oil of roses and oil of bitter almonds. Although several thousand kinds of roses are raised, practically the only one that comes under notice for the winning of the oil is the *Rosa damascena*, Mill., which is cultivated in Bulgaria, Turkey and in Germany (near Leipzig). In South France *Rosa centifolia*, L., is used for the preparation of rose water and rose pomade. The delicate characteristic smell of rose oil (attar of roses) is caused, less by the chief constituent geraniol, than by other substances, such as *l*-linalool, *l*-citronellol, nerol, phenylethyl alcohol, citral, *n*-nonylaldehyde, eugenol and an aliphatic sesquiterpene alcohol $C_{15}H_{26}O$, which is apparently identical with farnesol.

To the family of the *Myrtaceæ* belongs the evergreen clove tree *Eugenia caryophyllata*, Thunb., whose buds are known in commerce as Zanzibar cloves, and which yield a very much used spice. The cloves contain 15 to 18 per cent. essential oil, the chief ingredient of which eugenol, $C_{10}H_{12}O_2$, is not only used in medicine and perfumery, but above all for the preparation of vanillin. For this purpose the eugenol is transformed into the more easily oxidisable *iso*eugenol by the action of alkalies, a substance which forms the basis of the odoriferous substance contained in the garden pink, *Dianthus Caryophyllus*, L.

The oils of more than 160 species of the genus *Eucalyptus* have been distilled in Australia, and their chemical constituents examined. One of the most important of these bodies is cineole, $C_{10}H_{18}O$, also called eucalyptole. It is contained in great quantities in the oils of *Eucalyptus polybractea*, R. J. Baker, and *E. Smithii*, R. J. Baker. At ordinary temperature cineole is an optically inactive fluid, crystallising at about +1°C. Cineole takes an exceptional position amongst the constituents of the essential oils in so far as it is an organic oxide according to its composition. By its use in the smelting

industry, for the flotation process, the oil of *Eucalyptus dives*, Schau., has more than any other become important. 300 tons of oil are annually used in the De Bavary process for the separating of ores[1]).

A great number of harmless as well as narcotic aromatic plants belong to the *Umbelliferæ*: a special characteristic of this family is, that the aromatic substances do not occur in single organs, but are spread throughout the plant. Anisaldehyde (*p*-methoxybenzaldehyde), known by the name of "aubépine" is obtained by the oxidation of anethole (*p*-propenylanisole) which is present in large amounts in oil of aniseed and fennel oil. Since "aubépine" possesses in a high degree the odour of flowering hawthorn, it forms the basis of all artificial hawthorn perfumes. The unsaturated ketone carvone, $C_{10}H_{14}O$, the chief constituent of caraway oil possesses the characteristic property of forming a crystalline compound with sulphuretted hydrogen, from which it can be again separated in a pure state. The crystalline apiole, a dimethoxymethylenedioxyallylbenzene is the chief constituent of parsley oil, *Petroselinum sativum*, Hoffmann, only distinguished from the myristicin of nutmeg by possessing an extra methoxyl group. Myristicin itself has been found in a French parsley oil poor in apiole. The cultivation of *Carum Ajowan*, Benth. and Hook., an annual umbellifera, is very widely spread in India, whose finely divided seeds on distillation yield 3 to 4 per cent. of oil, which contains 40 to 50 per cent. thymol.

Amongst the *Ericaceæ* together with the beautiful rhododendron and the sweet smelling "ground shrub" *Epigœa repens*, L., is found wintergreen, *Gaultheria procumbens*, L., whose leaves yield the strongly aromatic oil of wintergreen. The really genuine wintergreen oil is hardly to be obtained in trade, since it has been almost completely substituted by the oil obtained from the birch bark of *Betula lenta*, L. The chief constituent of this oil, methylsalicylate, occurs in very many plants, as tea and coca leaves, in the blossoms of the tuberose and "meadow sweet flowers" (*Spiræa Ulmaria*, L.). Another ester of salicylic acid — amylsalicylate — which has not yet been found in nature, is very much used in perfumery. This strongly aromatic liquid smells like some of the *Orchideæ*, and is said to from the basis of artificial clover perfumes.

The family *Labiatæ* is very rich in plants containing essential oils. Schimmel & Co. recently found in Japanese peppermint oil a new interesting compound, a hexenylphenylacetate[2]) of the constitution

$$C_6H_5CH_2CO_2CH_2CH_2CH : CH \cdot CH_2CH_3;$$

recently van Romburgh[3]) pointed to the presence of this substance in the oil of tea leaves. Besides occuring in the *Umbelliferæ Carum Ajowan*, Benth. and Hook. thymol is also found in many of the *Labiatæ, e. g., Monarda punctata*, L., *Thymus vulgaris*, L. and in species of *Ocimum, Satureia, Origanum*. In the oil of *Monarda fistulosa*, L. the so-called wild bergamot, there is, together with carvacrol, an isomeride of thymol, thymohydroquinone, $C_{10}H_{14}O_2$ present, whose dimethylether forms the chief constituent of arnica root oil (*Arnica montana*, L.).

The large family of the *Compositæ* contains comparatively few plants with important perfume-substances. Chamomile, milfoil, and wormwood oils are notewortly on account of their deep blue colour. This coloration is caused by the unsaturated hydrocarbon $C_{15}H_{18}$, azulene, which has a faint odour of phenol and contains four ethylene linkings. On reduction, this tricyclic compound is transformed quantitatively into a tricyclic dihydrosesquiterpene $C_{15}H_{26}$. We must mention also Ngai camphor, consisting almost

[1]) Cf. *Report* April 1911, 72; October 1911, 49; April 1912, 79. — [2]) Cf. *Report* 1918, 39; Walbaum, *Journ. f. prakt. Chem.* II. 96 (1918), 245. — [3]) This *Report* p. 55.

entirely of *l*-borneol. Although camphor is more generally used in China, the Chinese place great value on this product got from *Blumea balsamifera*, DC. and besides using it for medicinal and ritualistic purposes, they employ it for perfuming the better kinds of Indian ink.

Power concludes his remarks with a short review of the essential oil industry in America. According to official reports[1]) there were 107 factories in the United States of North America in 1914 occupied in the manufacture of essential oils. The following table gives an idea of the quantities of essential oil obtained at that time in that country: —

	Amount	Value
Peppermint oil, crude	254793 lbs.	353076 $
„ „ purified	109198 „	248541 „
Spearmint oil	94209 „	238074 „
Birch bark oil	41178 „	67691 „
Wintergreen oil	6000 „	24538 „
Wormwood oil	4702 „	9040 „
Other essential oils[2])		348522 „

The total value of these products amounted to 1289482 $[3]). The total value of essential oils imported into U. S. A. from 1st July 1915 to 30th June 1916, amounted to 3109656 $[4]).

The amounts of camphor imported in the same period were: —

	Amount	Value
Raw Camphor	4574430 lbs.	11236172 $
Refined Camphor	1866154 „	619320 „

The essential oil industry in India. — Noteworthy advances have been made in the essential oil industry of East India and Ceylon since 1914. Whilst formerly sandalwood was disposed of by auction, the manufacture of its oil has now been started in Bangalore[5]). Thymol is obtained from ajowan seed in crystals[6]); the citronella oil industry is developing in Burma[7]), and palmarosa oil[8]) is obtained in the Melghat Division by means of steam-distillation.

Exports of raw material for the preparation of essential oils exported from East Indies in year 1917/18[9]).

	Quantity	Value
Ajowan seed	3960 cwt.	2735 £
Aniseed	1573 „	1065 „
Coriander seed	116273 „	80154 „
Cumin seed	18439 „	54778 „
Black Cumin seed	3379 „	5030 „
Dill seed	33813 „	28781 „
Cardamom	716358 „	64740 „
Cinnamon	55554 „	1064 „
Ginger	5841374 „	87254 „
Sandalwood	— „	56644 „
Lemongrass oil	26871 gallons	25613 „

[1]) *Census of manufactures for 1914 issued by the Department of Commerce* 1918. — [2]) Amongst these are to be counted, sassafras, cederwood, pennyroyal, tansy oils and considerable quantities of sandalwood, camphor, clove, parsley, patchouli, lemon and orange oils. — [3]) These figures do not take into account the turpentine oil industry. In 1914, 27648939 gallons of turpentine oil were prepared and were valued st 10740327 $. — [4]) *Yearbook of the Department of Agriculture* 1917. — [5]) Cf. *Report* 1919, 45. — [6]) Cf. *Report* 1918, 70. — [7]) Cf. p. 17 of this *Report*. — [8]) Cf. *Report* 1919, 37. — [9]) *Journ. Soc. chem. Industry* 38 (1919), R. 305.

The perfumery industry which has existed in India for two centuries has considerably decreased. In Gazipur, one of the head quarters of this industry, the annual turnover for essences and pomades in recent years is reckoned on the average as $1^1/_2$ lakhs = 150000 rupees[1]).

The scent-substances of roses (*Rosa damascena*, Mill.), jasmine (*Jasminum grandiflorum*, L.) and ginger- or geranium-grass (*Cymbopogon Martinianus*, Schult. and others, according to Burkill *C. Martini* var. *Motia)* were chiefly obtained and prepared. Whilst "Attars"[2]), flower-scents with a basis of sandalwood oil, are prepared more in Kanauj (Kanouj), a city in Oudh, between Cawnpore and Allahabad. In Gazipur we mostly find jasmine *(Chameli)* and palmarosa pomade *(Motia);* as well as rose-water, and less rose-oil. The pomades are obtained according to a method of "enfleurage" by means of sesame seeds[3]). After the seeds have been washed, husked and dried, alternating layers of seeds and jasmine flowers are laid one over another, and are left in this position for 12 to 24 hours. The flowers are then removed, and replaced by fresh ones. The pomade known as "siré ki tilli" is obtained from the perfume laden seeds with the help of a wooden press. A second-quality hair oil is obtained in the same way from the flowers that have been once used.

Since the district of Gazipur is not unsuitable for a cultivation of the plants, the perfume industry would again improve, provided that the manufacturers and growers were less negligent and more influenced by new ideas and methods.

The *Australian Government* helps the essential-oil industry to the extent, that it allows the manufacturers duty-free alcohol for the preparation of perfumes. The condition is that the alcohol, by the addition of essential oils (at least 2 ozs. per gallon) is denaturised. In addition to eucalyptus oil, lavender, bitter orange, bay, clove, lemon, geranium, rosemary, neroli, mandarin and sandalwood oils are obtained.

A series of artificial preparations are also prepared on this continent, as ionone, rhodinol, artificial rose, jasmine and neroli oils and are mostly used on the spot for perfumes and toilet soaps. The lavender oil, which is obtained from the lavender plant cultivated in Victoria is said to equal the Mitcham oil[4]).

Our cultivated and wild-growing spice plants.— The cultivation of spice plants, which had retrogressed of late years, has again received more attention since the war. Also in future it will be well to continue the cultivation in the kitchen garden, and to cultivate on a large scale aromatic plants in those parts of the country where the climate is favourable.

In a detailed work H. Ross and K. Bosshart[5]) have noted and discussed all the spice plants which grow here or are capable of being cultivated. The authors give a short botanical description of the individual varieties, and furnish details over the home, use and the cultivation of the following plants:—

Aniseed, *Pimpinella Anisum*, L.; (sweet) basil., *Ocimum Basilicum*, L.; artemisia, *Artemisia vulgaris*, L.; fenugreek clover, *Trigonella Fœnum-græcum*, L.; summer savory, *Satureia hortensis*, L.; borage, *Borago officinalis*, L.; dill, *Anethum graveolens*, L.; wild marjoram, *Origanum vulgare*, L.; southern wood, *Artemisia Abrotanum*, L.; tarragon, *Artemisia Dracunculus*, L.; fennel, *Fœniculum vulgare*. Mill.; garden cress, *Lepidium sativum*, L.; hyssop, *Hyssopus officinalis*. L.; calamus, *Acorus Calamus*, L.; chevril, *Anthriscus Cere-*

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[1]) *Perfum. Record* **10** (1919), 190. — [2]) Cf. *Report* **1917**, 31. — [3]) Cf. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 398. — [4]) *Chemist and Druggist of Australia*. From *Chemist and Druggist* **92** (1920), 746. — [5]) *Heil- und Gewürzpflanzen* **2** (1918/19), 183.

folium, Hoffm.; coriander, *Coriandrum sativum*, L., caraway, *Carum Carvi*, L.; lavender, *Lavandula Spica*, Loisel (*L. officinalis*, Chaix, *L. vera*, D. C.); lovage, *Levisticum officinale*, Koch; marjoram, *Majorana hortensis*, Moench (*Origanum Majorana*, L.); balm mint, *Melissa officinalis*, L.; horse-radish, *Armoracia lapathifolia*, Gilib. (*Cochlearia Armoracia*, L.); poppy, *Papaver somniferum*, L.; clove-wort or wood avens, *Geum urbanum*, L.; parsley, *Petroselinum sativum*, Hoffm. (*P. hortense*, Hoffm.); peppermint, *Mentha piperita*, L.; burned saxifrage, *Sanguisorba minor*, Scop. (*Poterium Sanguisorba*, L.); wild thyme, *Thymus Serpyllum*, L.; rue, *Ruta graveolens*, L.; rosemary, *Rosmarinus officinalis*, L.; sage, *Salvia officinalis*, L.; tone saffron, *Crocus sativus*, L.; sour sorrel, *Rumex* species; melilot weed, *Trigonalla (Melilotus) cœrulea*, Ser.; black caraway, or black cumin, *Nigella sativa*, L.; celery, *Apium graveolens*, L.; black mustard, *Brassic nigra*, Koch; white mustard, *Sinapis alba*, L.; soy bean, *Soja hispida*, Mœnch; Spanish pepper, *Capsicum* species; marsh marigold, *Caltha palustris*, L.; tomato, *Solanum Lycopersicum*, L.; garden thyme, *Thymus vulgaris*, L.; juniper, *Juniperus communis*, L.; woodruff, *Asperula odorata*, L.; wormwood, *Artemisia absynthium*, L.; cultivated chicory, *Chicorium Intybus*, L.; onion-like plants, *Allium*-varieties: kitchen onion, *Allium Cepa*, L.; winter onion, *A. fistulosum*, L.; chive, *A. Schœnoprasum*, L.; shalot, *A. ascalonicum*, L.; garlic, *A. sativum*, L.; pearl onion, *A. Ophioscorodon*, Don.; winter leek, *A. Porrum*, L.; summer leek, *A. Ampeloprasum*, L.

We find similar efforts to become independent of the important drugs from abroad also in countries outside Europe. As with us, great attention is being devoted to the *Cultivation of aromatic plants in America*, and every effort is made to encourage it[1]).

P. H. Todd[2]) pointed out in a lecture to the "Manufacturing Perfumers' Association of the United States" at New York, that with the tremendous extent of the United States, and the differences of climate and the varieties of soil, a suitable growing-district could really be found for every plant yielding aromatic substances. In many cases the question of expense alone would render doubtful a successful growing of aromatic plants. Up to now the following have been obtained in the United States of N. America not only for their own use, but also for export in large quantities:—peppermint, spearmint, pennyroyal, wintergreen, birch bark, sassafras, wormwood, tansy, erigeron oils and the hemlock-pine-needle, cedarwood, and pine-needle oils[3]).

The peppermint oil coming from South Michigan and North Indiana, is an example of the manner in which foreign processes of preparation, fromerly confined to European countries, have been adopted and simplified. In England the peppermint roots are allowed to throw shoots in spring. When the shoots have developed into plants of 2 to 3 in. high, they are transplanted at certain distances apart. In America on the contrary, the roots are planted in long furrows—made by a plough—3 ft. apart; which is a quicker and cheaper way. Whilst in England the average yield in 15 lbs. per acre, it amounts in America to at least 25 lbs. per acre. The English distil the herb over boiling water, and use several hours in a distillation. In a modern American establishment a larger amount of oil is distilled with direct steam in less than twenty minutes.

Of the essential oils obtained by America chiefly from Europe, the following for the needs of the perfume industry come under notice:—lavender, rose, rosemary, geranium, neroli, orris oils; and the following oils, prepared either by enfleurage or maceration:—jasmine, tuberose, jonquil, violet, hyacinth, &c.

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[1]) Cf. also *Report* November 1908, 154; *Report* 1918, 87. — [2]) *Americ. Journ. Pharm.* 91 (1919), 437. — [3]) Oils such as turpentine are meant; pine oil = *Kienöl*.

The lavender plant has already been successfully cultivated in Michigan. Damage is only caused by occasional falls of snow; hence it would be more advantageous to cultivate the plant in Carolina, where the weather in more favourable.

Roses indeed grow luxuriantly in California, but the air there is too dry, and the oil-yield would be small. East of the Mississippi however, the ground — as in Bulgaria — is sufficiently moist, and the climate not too hot, so that there, conditions for a profitable rose culture are at hand[1]).

Rosemary which above all grows in Spain and on the coasts of Dalmatia, would flourish excellently in the warm climate and on the chalky ground of Florida.

For the winning of geranium and neroli oil, the pelargonium species and bitter oranges — coming from Spain and southern France — could be just as easily cultivated in the warm south-eastern states of North America.

Orris species are successfully cultivated in California.

Up to now attention has not been paid in America to the large-scale production of essential oils from hyacinths, tuberoses, jonquils, jasmine, violets, &c. But there, plants have been cultivated for experimental purposes by the "Department of Agriculture" as well as in the gardens of the M. Todd Company in Mentha (Michigan). The winning of these products on a large scale is hindered by the high wages, for these products demand much hand labour.

A. Reclaire[2]) reports on *perfume containing plants occurring in Holland.* In addition to the cultivated plants — of which the caraway takes the first place — a series of wild aromatic phanerogams flourish in the Netherlands, which have not yet been made use of there for the preparation of essential oils. Amongst there may be mentioned: — the common juniper, *Juniperus communis*, L., *Coniferæ;* Dutch myrtle, *Myrica Gale*, L., *Myricaceæ;* calamus, *Acorus Calamus*, L., *Araceæ;* bear's breech, *Heracleum Sphondylium*, L., *Umbelliferæ:* wild thyme, *Thymus Serpyllum*, L., *Labiatæ;* origan, *Origanum vulgare*, L., *Labiatæ;* yarrow or milfoil, *Achillea Millefolium*, L., *Compositæ;* tansy, *Tanacetum vulgare*, L., *Compositæ: Artemisia maritima*, L., *Compositæ;* sea fennel or samphire, *Crithmum maritimum*, L., *Umbelliferæ.*

Noordwijk is said by C. de Graaff[3]) to be the centre of the *medicinal plant culture in Holland*, where people have been occupied in growing medicinal herbs since the end of the 16th century. The cultivation could not be maintained in Wassenaar, and at present only peppermint, licorice and roses are to a small extent grown there. On the contrary, the undertaking on Walcheren (Zeeland), established in 1917, continually increases. In the neighbourhood of Kondekerke, and in East-Kapelle the cultivation of valerian, peppermint, thorn apple, woodruff, iris, elecampane, wild thyme (or wild caraway), wormwood, witchhazel and hydrastis.

Cultivation on the Seychelles. — As is known, the vanilla plant, which 60 years ago was introduced into the Seychelles from Réunion, and was quickly naturalised on account of the favourable conditions, together with copra were the most important articles of export from this island group. But for some time there has been a great change noticeable in the exports from the islands. About 20 years ago, quantities of vanilla to the value of 1000000 rupees were exported; the value of the 1917 crop was only 50000 rupees[4]). The cause of this surprising backward movement must be ascribed

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[1]) We reported already in *Report* April **1915**, 40, on the possibility of cultivating roses in Oregon. — [2]) *Perfum. Record* **10** (1919), 289. — [3]) *Heil- und Gewürzpflanzen* **3** (1920), 201. — [4]) *Perfum. Record* **10** (1919), 186; cf. *Report* **1919**, 77.

first of all to the dry weather of 1904 to 1911, the exhaustion of the soil through the continued raising of the plants on the same land, and to the appearance of the *Calospora*-fungus (*C. Vanillæ*, Massee). Already in our *Report* **1915**, we stated that the existence of the vanilla industry on the Seychelles was threatened[1]) by the appearance of this fungus disease. It may also be said that by reason of the War vanilla has almost disappeared from the world market[2]).

In measure as the vanilla export declined, there developed several essential oil industries on the Seychelles: — ylang-ylang, vetiver, cinnamon bark, and cinnamon leaf oils. The distillation of cinnamom leaf oil[3]) especially, which has been carried on since 1907, has become a profitable source of income for the island. At present there are 17 distillation factories at work, each preparing 45 tons cinnamon leaves monthly, with a yield of 4 to 8 kgs. of oil per ton.

"Perfumes of the mineral kingdom" is the title of an essay, in which H. Heller[4]) discusses the odoriferous substances occurring in many minerals. Since minerals in a narrow sense — inorganic minerals — are odourless, all the scents of the mineral kingdom must be traced back to substances developed during their examination (sulphur and arsenical compounds), or else must be ascribed to organic admixtures. Thus the pleasant smell of the violet stone arises from a species of algæ which covers the mineral with a layer scarcely visible to the eye. The smell impression of metals, flints, and all clayey smells are caused by absorbed impurities (gases, products of secretion of our hands, as sweat, epithelium). Amongst minerals with names such as *Stinkschiefer* (stink slate), *Stinkfluss* (fetid fluorspar, bituminous fluorite), *Stinkquarz* (fetid quartz, bituminous quartz) the impurity occurs as bitumen. The *Stinkfluss* found at Wölsendorf in Bavaria, as a matrix of calcium fluoride in granite, contains 0.02 per cent. hydrocarbon according to Wyrouboff.

Several essential oils are still used in *micro-technology* for media or intermedia; further as solvents for colours, or similar purposes. For the role they played in this respect, especially formerly, they must thank their own good qualities less than the historical development of micro-technology, or even chance. At least this is the view of P. Mayer, who, in his work "On the Volatile Oils and their Substitutes"[5]) points ont, that with the exception of cedar-wood oil, all volatile oils can be advantageously replaced by simple chemical bodies.

First in the beginning of the 50th year of the 19th century, when textile fabrics began to be colored, a volatile oil — oil of turpentine — was used to convert preparations from alcohol into balsam. Shortly afterwards oil of aniseed and oil of cloves were used for the same purpose. Only considerably later were lavender oil (1883), oil of thyme (1886), oil of rosemary (1887?), linaloe oil (1898) and peppermint oil (1912) adopted. Nevertheless in 1912. P. G. Unna and L. Golodetz[6]) enumerated about 30 oils in the list of brightening mediums which are of importance in their reaction on rongalite white and chrysophane yellow. As chief representative of the strongly oxidising oils in manufactures oil of cloves must be placed, and as the chief reducing oil, oil of turpentine. In staining sections when colouring with methyl green and pyronine, clove oil and rosemary oil are important. On account of their efficacy as brighteners,

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[1]) Cf. *Report* October **1915**, 68. — [2]) Cf. *Report* **1919**, 77. — [3]) Cf. *Report* April **1919**, 18. — [4]) *Deutsche Parf. Ztg.* **6** (1920), 92. — [5]) *Zeitschr. f. wissensch. Mikrosk. u. f. mikrosk. Technik* **36** (1920), 219. As per kindly forwarded special reprint. — [6]) The significance of Oxygen in dyeing. *(Die Bedeutung des Sauerstoffs in der Färberei.) Dermat. Studien* **22** (1912).

amber, calamus, cananga, citronella, caraway, nutmeg, bitter orange, rue, savin, mustard and juniper-berry oils are named "the transparence-producing oils".

In addition to these oils noted only by Unna and Golodetz, 19 other oils were up to now used in micro-technology, of which lemon, eucalyptus, fennel, lavender, rosemary, peppermint, sandalwood, spike, and thyme oils can be dispensed with entirely, and need be no more mentioned.

Oil of aniseed on account of its high refractive index, is used for examining or preserving many less transparent or strongly refractive objects, dental enamel for example.

Oil of bergamot is suitable for collodion sections, since the sections then flatten, become stiff, but do not however, contract. Oil of bergamot is also recommended as intermedium for paraffin.

Cajuput oil is used for colouring the *Tigroids* (Nissl's bodies) in the ganglia cells according to the method of F. Nissl, and dissolving celloidin according to the process of Carnoy and Lebrun[1]).

Cedarwood oil concentrated (thickened) till its refractive index = 1.515 serves as medium; in viewing a preparation with immersion lenses, no cover slip is needed. Further, small objects can be cut up in the oil and preserved. According to P. Mayer cedarwood oil renders good service in testing the purity of coal-tar dyes, since they are mostly insoluble in it.

Gaultheria oil (oil of wintergreen) is used for thinning Canada balsam, as intermedium for balsam and paraffin, and also as a medium. Mayer was able to preserve unaltered a specimen coloured with "Hämalaun" in the oil.

Linaloe oil is very good to use in order to transfer objects from alcohol into balsam, since it does not dull like oil of cloves, but remains colorless.

Oil of cloves has been more used than any other oil, especially as intermedium for balsam, or also as medium. It is often used for dissolving aniline dye stuffs, for the purposes of staining, or to extract over-staining.

One has found use for origanum oil in the double inbedding in celloidin and paraffin, and in making sections lighter coloured.

Already in 1834 oil of turpentine was used by A. Retzius to increase the transparency of paper-thin laminæ of teeth, which laminae had been prepared with the aid of file and saw[2]). The oil is now used to thin balsam, to dissolve rosins (colophony, dummar) since these harden much more slowly than when dissolved in xylene and chloroform. Strasburger and Koernicke use oil of turpentine as medium for algæ; as a medium for aniline dyes, resinised or ozonised oil of turpentine is praised by P. Ehrlich and W. Rubaschkin.

Cinnamon oil with its much higher refractive index than that of balsam or resin, is used with advantage instead of oil of cloves as intermedium or medium.

The various sorts of micro-technique (paraffin-, celloidin-, ice-, gelatine-, and rosin-technique), which are exhaustively described in Mayer's work, cannot be gone into further here.

Only a few volatile oils are suitable as media for permanent preparations. Most of them evaporate too rapidly or deteriorate under the cover glass. The only exception is cedar-wood oil. It is similar to balsam in that it resinifies and thickens in lying long under the cover glass; at the same time its refractive index approximates to that of glass, which is of special importance in making observations with immersion lenses.

[1]) *Cellule* **13** (1897), 71. — [2]) *Arch. f. Anat. u. Phys.* **1834**, 487.

All the superfluous above-mentioned essential oils are advantageously replaced by suitable synthetic compounds. Methylsalicylate can replace gaultheria oil. Methylbenzoate has rendered oil of cloves practically superfluous, and cajuput oil is replaced by cineole. Pinene takes the place of turpentine oil, and cinnamic aldehyde is used instead of cinnamon oil. Origanum oil is replaced by carvacrol[1]); finally oil of bergamot is still indeed considered necessary on account of its apathy for celloidin sections; but has in Mayer's opinion, become unnecessary through the employment of "carboxylene".

Bibliography.

Medicinal Literature of the Middle Ages. — As a useful reference book in studying the medical literature of the middle ages the *„Leitfaden für Arzneibereiter"* (= Guide for Pharmacists) by the Italian doctor Saladin of Ascoli, translated into German by L. Zimmermann[2]), can be recommended. This work, composed in the middle of the 15th century, gives in a compressed form a good idea of the pharmaceutical knowledge of that time. Technical expressions, weight, measure, directions for collecting and preserving drugs are explained in the summary. There is, in addition, a collecting-calendar, and a complete name and subject index contained in the "Guide"[3]).

Analytical Notes.

Viehoever[4]) gives some data on the attempts to estimate the essential oil in spices and drugs. According to most methods, frequently modified, the drug is steam-distilled and the oil obtained from the distillate saturated with common salt, by shaking up thoroughly with a volatile solvent. All these processes[5]), already described and discussed by us, yielded no exact results, since the sources of error in getting rid of the solvent are unavoidable. On the contrary, Viehoever thinks he can arrive at better results if he mechanically separates the oil and water in the distillate, and calculates the percentage content from the volume and specific gravity of the oil. In the *Report* of April **1914**, p. 120, we have discussed a method depending on the same principle, according to which P. C. Chattopadhyay, with the aid of an apparatus called "Tailameter", has estimated the volatile oils in plants and spices. In many cases this method gives useful results.

Utz, who for years[6]) has stood up for the employment of the refractive index in the investigation of essential oils, has yet again published a small "study" in this subject[7]). The chief value of this diligent work consists in the classification — not absolutely complete — of the literature belonging to the subject, whilst the publication of the refractive indices of a large series of oils determined by Utz will only tell us little, for it is by no means certain that he had really pure oils, and he was hardly in the position to convince himself in all cases of their faultless quality. In any case the observed values do not lie completely within the limiting figures determined by us, although they are set down in the tables. In order to show how the refractive index is influenced by admixtures Utz gives a comparison of the refractive indices of pure,

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[1]) Cf. *Report* April **1893**, 51. — [2]) *Salidini de Asculo serenitatis principis Tarentini physici principalis compendium aromatariorum.* Published by Dr. Zimmermann, Leipzig 1919. Publishing House J. A. Barth. Price 8 marks. — [3]) As per *Schweiz. Wochenschrift f. Chem. u. Pharm.* **57** (1919), 479. — [4]) *Journ. Assoc. of Official Agricult. Chem.* **3** (1920), 381. — [5]) Cf. *Report* October **1902**, 86; April **1910**, 43; April **1916**, 95. — [6]) *Apotheker-Zeitung* **15** (1900), 441, 453; **16** (1901), 742. — [7]) *Deutsche Parf.-Ztg.* **6** (1920), 25.

and correspondingly adulterated oils, but also here, leaves out the other constants, which is much to be regretted, for this would have shown if the refractive index really is so necessary in testing essential oils, as many people maintain. We have never denied that it may be of use in solitary cases.

Utz sums up his judgement as follows, "the finding of the refractive power furnishes us with an additional valuable means for recognising the purity or otherwise of essential oils, but it is not feasible however, to judge essential oils merely by reason of having determined their refractive indices". We should like to amplify the last remark by saying that the judging of essential oils solely according to the refractive index would in most cases be quite impossible.

The "Table of Refractive Exponents" which the optical firm Adam Hilger Ltd., London, has got J. N. Goldsmith to compile, may be regarded more as a publication for advertising purposes. It is discussed further in an English trade-paper[1]). We satisfy ourselves with the reference.

Besides ethyl alcohol, propyl and butyl alcohol are used in the preparation of alcoholic potash for *the estimation of saponification values*. Comparative experiments of A. M. Pardee, R. L. Hasche and Emmet Reid[2]) on fatty oils, fats and waxes shewed that butyl alcohol gives more exact values than ethyl alcohol, especially in the case of substances which are saponified with difficulty. Since the boiling point of butyl alcohol is in the neighbourhood of 116.8°, the saponification can be more effective on account of the higher temperature. It is to be assumed that butylalcoholic potash will also find advantageous employment in the analysis of essential oils, in order to saponify quantitatively esters only decomposed with difficulty, *e. g.*, salicylates, and above all valerianates. Years ago H. F. Slack[3]) recommended benzyl alcoholic potash for the ester determination of essential oils, but we think butyl alcohol is more suitable. In our opinion, the use of butyl-alcoholic potash must remain confined to difficultly saponified esters, on purely practical grounds, for the high boiling point of butyl alcohol renders the use of a water bath impossible, which would be a great hindrance to saponification on a large scale, which is the order of the day in the laboratories of our industrial branches.

With unsaturated bodies as limonene, pinene, &c., and the essential oils, the *iodine number* is influenced by the quantity of iodine used, and attains a maximum when the quantity of iodine present is from 13 to 17 times the quantity of oil under test. Hence by the iodine value of an essential oil is to be understood the maximum amount of iodine combined with 100 g. of the substance. If alcoholic iodine solution is used instead of the Hübl reagents, the amount of combined iodine is practically independent of the temperature between 15 and 45°, and proportional to the excess of iodine used. The constant so determined — the pseudo iodine value of the essential oils — is said to form, according to R. Huerre[4]) the same maximum amount of iodine, which combines with 100 g. of the substance dissolved in chloroform, to which has been added a great excess of alcoholic iodine, and which mixture has been allowed to stand for 2 hours at ordinary temperature.

We are still opposed to the determination of the iodine number in essential oils, for it can give us no information as to the quality of the oil[5]).

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[1]) *Perfum. Record* **10** (1919), 198. — [2]) *Journ. ind. eng. Chem.* **12** (1920), 481. — [3]) Cf. *Report* **1916**, 89. — [4]) *Journ. de Pharm. et Chim.* VII. **20** (1919), 216. As per *Chem. Zentralbl.* **1920**, II. 408. — [5]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 569.

In estimating the *essential oil in mustard-seed,* the way in which the sample has been macerated has an influence on the result. By a series of experiments, A. Viehoever[1]) determined the best way of treating the seeds preparatory to the actual oil estimation, and arrived at the following results:—

Too long a maceration (more than 2 hrs.) gives too low values. Raised temperatures, up to 37°, accelerate the process of fermentation. Addition of white mustard (*Sinapis alba,* L.) and of tartaric acid, and shaking during the maceration, have no influence on the result; on the contrary, addition of alcohol before the maceration, increases the quantity of oil set free.

For the test, the powdered seed was passed through a sieve of 1 mm. mesh; hence the addition of olive oil, which is said to prevent frothing, was unnecessary. According to Viehoever, the best condition is maceration for 2 hours at 37° (apparently without alcohol). The German pharmacopœia prescribes a 2 hrs. maceration at 20 to 25°. Viehoever mentions that the results obtained by the Röser method[2]) must be accepted with caution, since the directions can be wrongly interpreted.

Balsams. — On account of the literature and personal experiments, L. van Itallie brings forward new proposals as to how the sections in the Dutch Pharmacopœia dealing with copaiba, tolu, and Peru balsams might be modified. In so far as van Itallie's statements differ from the German Pharmacopœia, 5th edition, or mention something new, they are here reported[3]):—

Copaiba balsam. — d 0.960 to 0.996. A mixture of copaiba balsam, 1 vol., and light petroleum, 2 vols., must only be slightly cloudy (gurjun balsam). A mixture of 3 vols. copaiba balsam and 1 vol. aqueous ammonia must be neither cloudy nor milky (fatty oils), and ought also not to gelatinise after 24 hours. There should be no odour of turpentine oil on heating 300 to 400 g. balsam on the water bath. After evaporating the volatile oil a resin, which is clear and hard in the cold, must remain as residue (test for fatty oils and paraffins), whose weight ought at least to amount to 45 per cent. of the quantity used. If the volatile oil in about 25 g. copaiba balsam be completely distilled over in steam and dried with dried sodium sulphate, the rotation in a 10 cm polarimeter tube should be not less than —7° (test for African balsam). The acid value, determined similarly to those of the fatty oils, ought to lie between 75 and 85. The saponification value ought only to differ by 14 units from the acid value.

Peru balsam. — The balsam is obtained from *Myroxylon Pereirœ,* Klotzsch. d 1.145 to 1.180. On warming, the balsam ought not to smell of turpentine oil, copaiba balsam, or storax; and after half an hour it should have lost 2.5 per cent. of its weight at the most. A mixture of 3 vols. of Peru balsam with 1 vol. of carbon disulphide ought to be clear (test for artificial balsams). On shaking together 5 drops of Peru balsam with 8 cc. light petroleum in a tube, the balsam should settle on the walls of the test-tube as a sticky mass. The light petroleum must contain no powdery constituents. On pouring off and evaporating the light petroleum, and decomposing the residue with one drop of concentrated nitric acid (d 1.4) a yellow colour should appear, but no blue or green (test for artificial balsams). The acid value should amount to 56 to 80. The balsam must contain 55 to 80 per cent. cinnamein, whose saponification value is not under 235, when determined as with fatty oils.

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[1]) *Journ. Assoc. of Official Agricult. Chem.* **3** (1920), 381. — [2]) Cf. *Report* October **1902**, 52. — [3]) *Pharm. Weekblad* **56** (1919), 1185. As per *Chem. Zentralbl.* **1919**, IV. 582.

Tolu balsam. — The balsam is obtained from the wounded trunks of *Myroxylon toluiferum*. H. B. and K. The residue after evaporation, obtained by digesting 1 g. balsam with 20 cc. carbon disulphide and evaporation of the filtrate, is crystalline with a pure aromatic odour and taste, which do not remind one of turpentine oil and ought, when digested with 2 to 3 cc. ammonia solution, to yield a liquid, which has not gelatinised after 12 hours (test for resin). The acid value of the balsam ought to amount to 110 to 160, and the saponification value 160 to 210. On ignition 0.5 per cent. of ash, at the most, should remain.

For the *analysis* of *balsams*[1]) which, according to E. Fourneau, can be regarded as a mixture of resins and volatile esters, the esterification of the free acids *(alcoolyse)* is recommended by Fourneau and M. Crespi[2]). This process has the advantage over saponification, for it does not attack the resins, is performed quickly and easily, and permits the isolating of the acids as esters without great loss. The method of work was as follows: — 200 g. balsam were mixed with the same amount of alcohol containing 6 g. hydrogen chloride, and the mixture boiled for 6 hours. After neutralising with 7 g. sodium carbonate, the esters formed were steam distilled and taken up with ether. From the ether residue the esters could be obtained by fractional distillation, and the acids after saponification; both could then be identified.

Peru- and Tolu-balsam, storax and benzoin were treated in this way. Benzoic acid, cinnamic acid and styrene were found in the fractions of the Peru balsam. The high boiling residue from these fractions yielded on hydrolysis, together with cinnamic acid, a terpene alcohol, which probably was identical with the peruviol of Thoms[3]). The small amount of alcohol allowed of no farther testing. The ethyl ester of benzoic acid, the ethyl ester of cinnamic acid and a terpene hydrocarbon tolene[4]) were identified in the tolu balsam. In benzoin, benzoic acid and cinnamic acid were identified. Only cinnamic acid and cinnamic alcohol could be obtained from storax — benzoic acid and benzyl alcohol were completely missing. This fact supports the hypothesis on the formation of esters in balsams. When, in plants, the phases phenyl alanine, cinnamic acid, benzaldehyde, benzyl alcohol and benzoic acid are passed through, then storax is only found in those plants, in which the process only advances to the second stage. An oxidation of cinnamic acid to benzaldehyde does not take place.

Determination of the value of spirit of camphor. — Several years ago F. Wratschko[5]) in an exhaustive work showed that, from the specific gravity d_{15° and the refraction n_{D20° of spirit of camphor, the alcohol content, as also the camphor content, could be obtained in a simple manner with the aid of a table. Wratschko prepared 6 to 14 per cent. solutions of camphor in diluted spirits of wine, determined the specific gravity d_{15° and the refraction n_{D20°, and from this, with the help of the equations

$$d = \frac{d_1 \cdot p + (100 - p)\, d_2}{100} \quad \text{and} \quad n = \frac{n_1 \cdot p + (100 - p)\, n_2}{100}$$

he calculated the specific gravity and refraction of camphor. In the equations d, d_1 and d_2 stand for the specific gravity, n, n_1 and n_2 for the refraction of the solution,

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[1]) Ordinarily balsams are regarded as solutions of solid rosins in essential oils, or as a mixture of the same. Tschirch calls the French balsams *Benzoresins ("Benzharze")*, that is all resins which contain benzoic or cinnamic acid, or the acids derived from them. — [2]) *Bull. Soc. chim.* IV. 26 (1919), 386. — [3]) Cf. *Report* April 1914, 80. (Peruviol is impure nerolidol.) — [4]) Tschirch writes in *"Die Harze und die Harzbehälter"*, 2nd ed. p. 244: — "What the tolene of Deville and Kapp is, to which the formula $C_{10}H_8$, $C_{10}H_{16}$, or $C_{24}H_{36}$ was ascribed, I cannot say. Probably it was impure styrene". — [5]) *Zeitschr. d. allg. österr. Apoth. Ver.* 52 (1914), 286.

the solute and the solvent, p = per cent. content of the dissolved substance in the total solution. In this way the values for camphor $d_1 = 0.9499$ and $n_1 = 1.4535$ were established, and checked by control experiments, which then served as basis for the tables drawn up by Wratschko.

Wratschko also attempted to determine the specific gravity of camphor by finding the density of a water-alcohol mixture in which small pieces of camphor floated. The figure obtained d_{18^0} 0.9959, as Wratschko himself writes, must be too high, for camphor absorbs water; earlier were found for *l*-camphor d_{18^0} 0.9853 and for camphor $d_{4^0}^{20^0}$ 0.963[1]).

According to Utz, who was able to prove the utility of the refractometric method by his own investigations, the process is suitable for the estimation of the value of solutions of natural as well as of artificial camphor, and is specially valuable, since only a few drops are used in the process[2]).

Estimation of thymol. — Moles and Marquina[3]) have published a process for the estimation of thymol. The method rests upon the formation of the iodine compound, and is similar to the thymol estimation worked out by Kremers and Schreiner[4]). Sodium bicarbonate solution is used instead of a solution of sodium hydroxide. Since the paper we have contains no further details, we must refer the reader to the original.

H. Droop Richmond and W. T. T. Ainsworth[5]) prescribe the following for the ester estimation of *menthyl valerianate:* — "2 g. of the ester are saponified for 60 minutes with 10 cc. of a normal alcoholic potash solution, and then titrated with normal sulphuric acid. The neutral solution is shaken up with chloroform, added in successive quantities of 15, 10, 10, 10 cc. From the polarisation of the chloroform extract in a 100 mm. tube, the menthol content is calculated with the aid of the formula: —

$$\text{Per cent. menthol} = \frac{\text{angle of rotation} \times 25}{-59} \times 100.$$

6 cc. normal sulphuric were added to the aqueous solution, which was then made up with water to 100 cc. 90 cc. of this were distilled off. The distillate contains the whole of the valeric acid, which is estimated by titrating with $\frac{N}{10}$ KOH.

It is remarkable that, according to this prescription for the saponification of the ester, a one hour's boiling with such a small excess of potash solution should suffice, since the esters of *iso*valerianic acid are noted for the difficulty with which they are saponified. Thus the saponification of 1.5 g. menthyl*iso*valerianate with 60 cc. alcoholic $\frac{N}{2}$ potash was only completed after 6 hours' boiling[6]).

Estimation of nitrobenzene in commercial nitrobenzene. — Since the method up to now used for the testing of nitrobenzene by its specific gravity and boiling point is inexact and uncertain, Ch. Simpson and W. J. Jones[7]) have worked out a new process, by which the per cent. content of pure nitrobenzene in nitrobenzene can be rapidly and exactly determined. According to this method, the freezing point — a value dependent on the nitrobenzene content — is determined, and from this, with help of an equation or a graph, the value of the desired per cent. content is found.

The nitrobenzene under examination is shaken up in a test-tube with two drops of water till saturated, the test-tube is then placed in a larger one which is surrounded

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[1]) Cf. *Report* October 1912, 159. — [2]) *Pharm. Zentralh.* 60 (1919), 373. — [3]) *Anal. Fis. Quim.* 17 (1919), 59. As per *Perfum. Record* 10 (1919), 199. — [4]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 594. — [5]) *Chemist and Druggist* 91 (1919), 828. — [6]) Cf. *Report* 1917, 89. — [7]) *Journ. Soc. chem. Industry* 38 (1919), T. 325.

by ice. A thermometer with a range of 0 to 6° divided into $^1/_{10}$° and calibrated, together with a copper-wire stirrer are immersed in the test-liquid. The freezing point is found in the usual way. One of the following three equations serves for calculation, in which x = per cent. content of pure nitrobenzene in weight, t = freezing point of the water-saturated test-liquid.

I. For the raw product washed with water in order to get rid of acids:— $x = 90.2 + 1.87\,t$.

II. For the raw product after separation of the un-nitrated benzene by distillation on water bath:— $x = 89.0 + 2.11\,t$.

III. For distilled nitrobenzene:— $x = 90.0 + 1.91\,t$.

Absolutely pure nitrobenzene freezes at 5.70°, and when saturated with water at 5.22°.

Simpson and Jones arrived at the above equations, in preparing, ten at a time, mixtures of pure nitrobenzene with the substances contained in raw nitrobenzene (paraffin, carbon disulphide, benzene, *m*-nitrobenzene, toluene, *o*-nitrotoluene, *p*-nitrotoluene), and then found their freezing points after saturating with water.

The process is also applicable to poor-quality products, when the sample is mixed with a sufficient quantity of pure nitrobenzene in order to bring the freezing point of the mixture above 0°.

The evaluation of nitrobenzene by means of its freezing point is by no means new. We have used these constants for years, and have found that the freezing point of a good commercial sample lies between +5 and +6°, if cooled to 0°, and then a little solid nitrobenzene is introduced.

Re testing of, and water- and oil-estimation in, *raw camphor* see p. 67 of this *Report*.

Physical Notes.

A treatise by T. H. Durrans[1]) supplies a long-felt want for a small text-book on distillation. He relies greatly on the work of C. v. Rechenberg[2]), partly in open quotations, partly also without acknowledging the source. Especially, the great laboriously compiled tabulated work of the boiling points corrected for normal pressures has been incorporated without mentioning whence it comes, which is all the more astonishing since the preceding and succeeding table bear references to their origin. In order to keep in agreement with the tables the author brings a wished-for supplement side by side with v. Rechenberg, by the incorporation of a table of heats of vaporisation and of specific heats of the substances coming under notice.

In his introductory remarks, the author seeks to rid his readers of the fear of the numerous formulæ and graphs by saying that the art of distillation has now been raised to the rank of an exact science, which finds universal technical application, and, at the same time is a subject for further investigation; a happy way of describing the importance of his text-book on distillation. The history of the vapour pressure formula, the corrections for deviations from normal pressure, also the chapter on constitution and boiling point, as well as Dalton's law of partial pressures, are here appropriately and clearly reproduced. The author has made the great chapter on steam distillation and fractionisation a labour of love; in it he has collected all available

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[1]) *Perfum. Record* **11** (1920), 154. — [2]) *Theorie der Gewinnung und Trennung der ätherischen Öle durch Destillation. (Grundzüge einer allgemeinen Destillationslehre.)* 1910. = Theory of the Winning and Separation of the Essential Oils by Distillation. (Outlines of a Universal Distillation-Science.)

experiences. In the mentioning of the book by S. Young, a few remarks might have been devoted to the work of v. Rechenberg, instead of finding his name in a foot-note to two tables, or in the list of abstracts of the periodicals.

The practical part is incomplete, but the author refers to a work of Parry already at hand. Here also, he endeavours to keep critical, and give the latest advances. Specially noteworthy is his demand, following v. Rechenberg's lead, for pressure measurements at the same point of the apparatus at which the temperature measurements are taken.

The book concludes with a small selection of practical laboratory apparatus for distillation purposes.

In addition, a half practical, half theoretical work of N. V. Sidgwick[1]) must be mentioned. He investigated the volatility of several organic acids of high boiling point in the steam current, and made use of the figures obtained in titrating the distillate, in determining the vapour pressure of the substance in question; his results are reproduced in the following abstract.

Substance (* fluid under water at 100 °)	Temperature at 760 mm.	Weight-percentage of acid in distillate	Vapour pressure in mm. × 10^2	Solubility in weight-percentages[2])	Distribution coefficient × 10^6 of the acid between steam-phase and saturated solution
*Benzoic acid	100.12°	1.006	112.9	8.0	73.9
*Phenylacetic acid . .	100.16°	0.294	29.55	11.2	15.43
*β-Phenylpropionic acid	—	0.247	22.5	3.5	41.4
*o-Toluic acid	100.10°	0.964	97.0	2.97	191.0
*m- „ „	—	0.604	60.7	1.98	136.0
p- „ „	—	0.215	21.6	1.16	108.9
o-Hydroxybenzoic acid	—	0.400	39.7	6.45	36.5
m- „ „	101.06°	0.0015	0.149	36.9	0.024
p- „ „	100.91°	0.0003	0.030	33.5	0.005
o:3-Hydroxytoluic „	—	0.261	23.5	1.16	132.4
o:4- „ „	—	0.135	12.1	0.94	80.1
o:5- „ „	—	0.202	18.2	2.15	55.3
m:4- „ „	—	0.0196	1.76	4.36	2.64
p:3- „ „	100.17°	0.0008	0.072	5.25	0.090
o-Nitrobenzoic „	117.0°	0.0246	2.01	92.8	0.156
*m- „ „	100.10°	0.0085	0.70	10.5	0.479
p- „ „	—	0.0017	0.096	0.29	2.38
o-Chlorobenzoic „	—	0.206	18.03	4.02	30.2
m- „ „	100.63°	0.225	19.70	0.5	260.0
p- „ „	—	0.0515	4.50	0.11	275.0

The process then only yields exact values, if the substance to be examined has no considerable solubility in water at 100°, which condition cannot always be satisfied (cf. o-nitrobenzoic acid).

As for the vapour pressure formula appearing in his work at the same time:—

$$\log p = A - B/T$$

(p = vapour pressure, T = absolute temperature, A and B are constants of the substance),

[1]) *Journ. chem. Soc.* **117** (1920), 396. — [2]) Partly as per Flaschner and Rankin, *Sitzungsber. d. Wiener Akad.* **118** (1902) IIb, 695, and partly from experiments in author's laboratory.

it is only approximate, as the author himself admits. Warning must be given against a conclusion which the author draws, and which has appeared in the summary of Durrans[1]). Moreover, this formula is only a shortened form of von Bose's[2]). From the application of the formula to various substances, it appears that the object of steam-distillation in getting as much of the substance of higher boiling point than water as possible into the distillate, will be the better realised the higher the temperature, and hence the pressure chosen. In reality the temperature if of 100° is not the boundary which separates the substances in this respect, but their chemical nature conditions increase or decrease of the concentration as is explained in the work of v. Rechenberg[3]).

The important subject of *standardisation*, for long employed in mass production as a time- and energy-saving device, has recently been taken up with regard to laboratory apparatus and has led to a first report of the Standardisation Committee of the Society for Laboratory Apparatus[4]). Up to now, one had been advised to procure a greater supply of apparatus — of a certain flask, for example — if one laid value on a fitting substitute, but in future this will be unnecessary, because exactly dimensioned articles of daily use in the laboratory will be on sale throughout the whole of Germany. In connection with this standardisation come comparative investigations for deciding the effectiveness of glass apparatus, *e. g.*, condensers and fractionating columns, as they are taken up in a manner worthy of thanks by F. Friedrichs[5]), in a series of works in Germany and by others in foreign countries. Here Friedrichs clears away many a prejudice, and proves experimentally, *e. g.*, with regard to fractionating columns, that the old Hempel column (a tube filled with glass marbles) still approaches nearest of all to the theoretical efficacy, whilst the numerous other constructions either do not possess in the slightest degree the qualities ascribed to them by their inventors, or are far behind the Hempel column in efficacy, which column only has one disadvantage — with small quantities of substance it retains too much of it. In this respect a successful improvement by Dufton[6]) appears to be appropriate. His fractionating column is such that the cylindrical space between two glass tubes is provided with a wire spiral, along which the condensed substance flows down, and the vapours ascend in constant contact with it. Indeed the cross-section and hence the efficiency appears lessened in comparison with the external circumference of the apparatus, so that, as it is, it cannot be recommended for larger quantities. At the same time the quantity of liquid retained by the column is reduced to a minimum. The author points out that the column works excellently with small quantities (10 cc.). The apparatus has only the disadvantage that in its construction, a metal wire is used, which may be attacked chemically. Here the application of the principle of the glass spirals introduced by F. Friedrichs might be appropriate.

A fractionating column, proposed by F. Friedrichs[7]) by reason of the results of his investigations with various constructions, in which the principle of the constant condensing temperature as stated by Hahn[8]) is applied, is indeed just as efficient as the Hempel column, but is excelled by this in the simplicity of its manipulation.

Another new fractionating column is due to M. H. Robert[9]). The lower part consists of a glass tube with constrictions filled with small glass rings of the Raschig system, (without stating the name of the inventor!) in a sealed-on, evacuated glass jacket. The middle part is a ten-bulb-tube in a glass jacket, through which a stream of air may

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[1]) *Zeitschr. f. physik. Chem.* **80** (1907), 944. — [2]) See above. — [3]) P. 354. — [4]) *Zeitschr. f. angew. Chem.* **33** (1920), I. 105. — [5]) *Ibidem* **32** (1919), I. 340; **33** (1920), I. 29. — [6]) *Journ. Soc. chem. Industry* **38** (1919), T. 45. — [7]) *Zeitschr. f. angew. Chem.* **32** (1919), I. 340. — [8]) *Berl. Berichte* **43** (1910), 419. — [9]) *Compt. rend.* **168** (1919), 999.

be passed for cooling purposes. The upper part is a neck after the style of Kahlbaum (the author gives a French name!) for the thermometer.

This publication becomes useful in furnishing a method of measurement of the efficiency of fractionating columns, which indeed, on its practical side, is not so thoroughly built up as that of Friedrichs, but which however in the formulating, offers something new. The method consists in this, that in keeping up of a certain rapidity of distillation (one drop per second) equal fractions are collected and examined. If one starts with a certain quantity of a normal mixture of benzene and toluene with v g. benzene and finds in the first half distillate a g. benzene and b g. toluene, then the efficiency figure runs thus:—

$$E = (a - b)/v.$$

In cases of excellent efficiency the expression approximates to unity, in cases of poor efficiency, to zero. It is not applicable to all numerical relations, of which one can easily convince himself, but only for a 50 per cent. starting material.

The Hempel column is so modified by W. Elsner[1]), that polished and finely-etched glass marbles (beads) of various sizes are placed above one another in layers. Probably the amount of liquid retained is smaller, but the raised price and the increased trouble both stand in no proportion thereto. Further, in Elsner's construction, the uncontrollable jacket cooling is replaced by a reflux condenser with cooling coil and filled with glass beads. This is really completely correct, only a special distribution-spray seems quite superfluous with laboratory apparatus.

Further, the following contributions on laboratory practice will have an interest here. Houben[2]) alters the Erdmann[3]) process of vacuum distillation in an atmosphere of CO_2, by using a receiver cooled with liquid air in such a manner, that he—as usual in vacuum distillations—uses a "boiling-capillary" but feeds this also with CO_2. The author remarks that the attained high vacuum is in no way deteriorated by this. Since the manometer is joined on next to the condensation apparatus and not to the distillation flask itself, the conclusion is false, as may also be the statement of the pressure (0.12 mm. Hg).

E. Lenk has devised[4]) a fractionating flask provided with two fractionating columns for the distillation of foaming liquids; the lower is provided with an efficient reflux condenser; the upper is joined to the receiver by a usual distillation tube; both can be evacuated over a three-way tap. The condenser is turned on first. As a rule the foaming ceases when real boiling begins, and one can reverse in the usual way, and further distil.

A further improvement consists in the shortened manometer for vacuum distillation. H. T. Clarke[5]) proposes that a hook-formed capillary should be fused in the closed limb, as is used in exact barometers. By this means, the inrush of air and steam on the one hand, and on the other hand the all too rapid falling of the mercury on disconnecting, probably leading to a shattering of the apparatus, could be avoided.

In our previous *Report*[6]) we had placed in view the publication of experimental principles for measurement of pressure in vacuum distillations. In the meanwhile these works have appeared[7]). The problem was solved in two sections:—first the pressure conditions were tested in the part of the boiling apparatus from the upper part of the boiling tube to the branch behind the receiver; and then the temperature and pressure relations in the boiling tube itself.

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[1]) *Chem. Apparatur* 7 (1920), 3; *Chem. Ztg.* 44 (1920), 11. — [2]) *Berl. Berichte* 52 (1919), 1460. — [3]) *Ibidem* 36 (1903), 3456. — [4]) *Chem. Ztg.* 52 (1920), 330. — [5]) *Journ. Americ. chem. Soc.* 42 (1920), 786. — [6]) *Report* 1919, 96. — [7]) C. v. Rechenberg and E. Brauer, *Zeitschr. f. physik. Chem.* 95 (1920), 184.

Only at higher pressures and with slower distillation does the pressure — generally read behind the receiver — practically correspond to the temperature observed at the boiling tube. The true saturation pressure is always higher; it increases

(1) with the narrowing of connecting tube from boiling tube to condenser,
(2) with decrease of the working pressure,
(3) with the increase of the distillation strength,

or in going back to the common cause of these three factors: — with the velocity of the vapour current in the connecting tube. How astonishingly high the velocity of the vapour can become, is shown by the following table. The figures denote metres per second! The amount of distillate in each case was 1 drop per second. Three various widths of connecting tube were inserted.

Distillation at:	760	20	6	2	0.1 mm. Hg.
Condenser tube 20 mm. wide:					
*Iso*safrole . . .	0.87	2.73	2.73	7.76	136
Water	0.18	5.67	17.8	50.5	—
Cooling tube 7 mm. wide:					
Dibenzylketone .	0.21	6.36	19.97	56.6	1002
*Iso*safrole . . .	0.24	7.09	22.29	63.4	1112
Water	3.14	46.4	145.2	412	—
Cooling tube 5.5 mm. wide:					
Dibenzylketone .	0.35	10.31	32.36	91.75	1620
*Iso*safrole . . .	0.39	11.49	36.1	102.7	1801
Water	5.09	75.2	235.3	669	—

All vapour velocities over about 10 m/sec must lead to noticeable "choking back", *i. e.*, the raising of the pressure in the boiling tube; in such cases also, reading off the pressure behind the receiver is decidedly faulty. That the mistakes occasionally can be greater than even the pressure read off, is not astonishing after this.

In the boiling tube, temperature differences indeed were observed, but no differences in pressure were present, not because no pressure differences were there, but because no sufficiently sensitive measuring method could be applied. For below 20 mm. working pressure, a difference of 1° in temperature corresponds only to 0.3 mm. and less, difference in pressure.

The final results of the investigation, and its discussion in connection with the investigations of Hansen[1]) is expressed as follows: —

"It has again become clear, that in the dynamical process of boiling point determination, not only the first source of error coming into one's mind is to be attended to — which has finally led to the demand, to measure the boiling pressure at the point where the boiling temperature is read off. Rather it is seen that in observing this condition in boiling point investigations, under certain conditions (very low pressure, high vapour velocity) it is not further possible to effectively determine the equilibrium of liquid and vapour thermally and volume-energetically. In other words there is no infallible determination of the boiling point according to the dynamic process, but it can still only be a matter of knowing the limits of accuracy of the method used, and to keep them below a certain order of magnitude."

The following rules are recommended for the practical carrying out of the dynamical boiling point estimation: —

[1]) *Zeitschr. f. physik. Chem.* **74** (1910), 65.

(1) The flask may be of glass or of metal. In the latter case a flat bottom is useful; with glass, a special side tube provided with glass capillary tube should be sealed on.

(2) The fractionating column must be provided with an appropriate Kahlbaum steam jacket.

(3) The neck of boiling flask must be at least 20 mm., the connecting tube to condenser, as also the condenser tube, be at least 15 mm. diameter.

(4) The thermometer bulb must be well within the steam jacket but 50 mm. above the spherical space of the distilling flask; the mercury thread must be always in the vapour.

(5) The measuring of the boiling pressure must be made in the boiling tube.

(6) The manometer must have limbs 15 mm. wide and stand exactly vertical.

(7) A boiling pressure of less than 5 mm. Hg is to be avoided.

(8) The rapidity of distillation must not exceed 1 drop per second.

(9) Only read temperature and pressure, when about 10 cc. have been distilled over (charge 50 cc.).

In a further work von Rechenberg[1]) goes back to the vapour pressure law of U. Dühring[2]). If t_1 and t_2 be the boiling points of a substance at pressures p_1 and p_2 respectively; and if ϑ_1 and ϑ_2 the boiling points of a second substance at the same pressure, than, according to Dühring:—

$$\frac{t_1 - t_2}{\vartheta_1 - \vartheta_2} = \text{constant.}$$

The author has now found that this formula is strictly valid when one only takes into account the pure distillation process; *i. e.*, the splitting-off of monomolecules from the liquid complex, without the occurrence of polymerisation in vapour and liquid. In other words, the formula of Dühring is a similar limiting law to the volume law of Mariotte-Gay-Lussac, and of similar fundamental significance.

In its numerical evaluation, this law experiences limitations by the mentioned appearance of polymerisation of the vapour; but the conditions of the fluid complex also influence the vapour formation and therewith the unlimited validity of Dühring's law. It is further seen that no simple formula can be found capable of reproducing the character of a given vapour pressure curve throughout its whole course. Indeed continually unsuccessful attempts are made to this end[3]); but certain factors combine, and also partly influence each other — at least at higher pressures and temperatures, so that the expression of the phenomena by means of a formula is impossible. Only that part of the curve free from dissociation follows the simple law of Dühring.

The author now finds that nevertheless not a simple type is present, but that there are two chief types of vaporisation. Water represents one type, n-hexane the other. Very similar to the water curve are:— oxygen, nitrous oxide, phosphine, hydrogen chloride, CO_2, cyanogen, and of organic compounds:— the acids, the fatty mono- or poly-alcohols, and the unsaturated fatty compounds with triple bonds, *e. g.*, acetylene; not, however, the aromatic and above all the cyclic alcohols and not the phenols, the tertiary alcohols and the unsaturated fatty alcohols, which like all other organic substances agree with the hexane curve. The author was able to illustrate the outstanding validity of the law of Dühring by several examples (the experimental groundwork of which originated in our physico-chemical department), which even excels the validity of the Ramsay-Young rule[4]).

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[1]) *Zeitschr. f. physik. Chem.* **95** (1920), 154. — [2]) *Wied. Annalen* **11** (1880), 168. — [3]) Compare, for example, P. B. Williamson, *Chemical and metallurgical Engineering* **22** (1920), 1151. — [4]) *Zeitschr. f. physik. Chem.* **1** (1887), 289.

Whether the two different outstanding types of vaporisation curves can be combined into a single one — the hexane curve — in view of the condition that in general, only relatively few substances follow the water-type, is discussed by the author, and declared to be possible.

In order to render easy the use of the Dühring law, the author further gives an exactly calculated table of the hexane vapour-pressure curve.

A final chapter is devoted to the (imaginary) zero point of vaporisation, which can be obtained from Dühring's formula for each substance, if it is assumed that that of water lies in the neighbourhood of — 273° C. The calculation of these new constants stands or falls with the certainty of this assumption; their true value is a matter of considerable uncertainty and even their theoretical and practical utility appears limited; thus whether, for example, the vapour pressure of glycerin at 27.9° C. is exactly zero or merely immeasurably small, has no practical bearing, and important theoretical inferences, perhaps about the molecular constitution of matter in connection with the latest ideas of Rutherford, Bohr, Sommerfeld, &c. does not come into the question.

C. Neuberg[1]) reports on "hydrotropic" phenomena. By "hydrotrophy" the author means the property possessed by numerous salts of considerably increasing the solubility of substances difficultly soluble, or insoluble, in water. In this sense the following substances for example are hydrotropic: — salts of benzoic acid, of benzene-sulphonic acid, of naphthoic acids and their derivatives, of thiophene-carboxylic acid, of pyromucic acid, of phenylacetic and similar aliphatic-aromatic acids, and of the acids of the hydroaromatic series. Hydrotrophy is manifested by the foregoing substances towards water-insoluble substances of many differing types, as hydrocarbons, alcohols, aldehydes, ketones, esters, nitro-compounds, bases, alkaloids, proteins, dye-stuffs, starches, and fats.

In general hydrotropic substances are of the nature of salts. The kind of cation has no essential importance, since the potassium, sodium, and lithium salts (of the same acid) show equal capacities; the solubility in water of the salt is important, since in general the hydrotropic action is greater, the greater the concentration of the solution employed. It has not been possible to adduce any general law in regard to the nature of the anion; one must look for explanation in the first place to the formation of soluble double, and complex compounds; and it has in fact been possible in certain cases to isolate crystalline compounds from the aqueous solution.

These phenomena have considerable physiological importance and are of practical interest, for example, for bringing difficultly soluble medicines into suitable aqueous solution, for the suppression of the coagulability of albuminous substances.

In chemical analysis too, experiments are proposed, to show hydrotropic phenomena as valuable aids; since though as yet only benzoates, salicylates, and *iso*valerianates have been investigated, these salts have the property of bringing into solution, or hindering the precipitation of, magnesium carbonate, calcium carbonate, and magnesium phosphate.

Certain of these hydrotropic effects have been long known. von Wistinghausen[2]) describes an experiment in which oil diffused through a bile-soaked animal membrane into an aqueous bile solution. Otto[3]), and recently Wieland and Sorge[4]) have given further information as to the dissolving power of the bile-acid salts. Further, a patent

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[1]) *Sitzungsberichte der Preuss. Akademie d. Wiss.* Berlin 1916, p. 1034. — [2]) *Diss. Inaug. Dorpat*, 1851. — [3]) *Berl. Berichte* 27 (1894), 2131. — [4]) *Zeitschr. f. physiol. Chem.* 97 (1916), 1.

specification by Wieland[1]), gives a method for bringing into aqueous solution difficultly soluble, and insoluble substances, by means of the alkali salts of choleic acid and bile acid.

Semmler's[2]) account (quoted by the author) of the formation of a stable compound between camphor and salicylic acid, is hardly a case of hydrotrophy, since there is no aqueous solution; it forms, however, an addition to the explanatory addition-reactions collected by von Rechenberg in his book: *Theorie der Gewinnung und Trennung der ätherischen Öle durch Destillation*, p. 627ff.

The action of aqueous sodium salicylate in increasing solubility was first pointed out by Conrady[3]). Later, Duyk[4]), by shaking a sodium salicylate solution with a terpene, obtained a crystalline compound, which by solution in water or by long heating at 100° C. could be broken up again. In three further papers he described[5]) (a) the general properties of aqueous salicylate solutions in raising solubilites (b) the connection between the magnitude of the increase of solubility of numerous essential oils and their constitution, and (c) the use of the regularities thus found, in the separation of several ethereal oils. Wolf[6]) employed aqueous solutions of sodium and ammonium salicylate to dissolve freshly precipitated iron, aluminium, and copper hydroxide, Spaeth[7]) a 5 per cent. sodium salicylate solution for the extraction of dyestuffs.

The most extensive and general data come, however, from C. Neuberg[8]). An abstract of his researches is out of the question, but as an example of his methods and the type of phenomena investigated, we give the hydrotropic reactions of a nearly 40 per cent. aqueous solution of sodium benzoate.

Hydrotropic reactions of an aqueous sodium benzoate solution (200 g. sodium benzoate made up to 500 cc.)

1. 2.0 cc. pure amyl alcohol were dissolved by 1.0 cc. of the benzoate solution. The mixture tolerated the addition of 0.5 cc. H_2O; 1.0 cc. H_2O caused the separation of an oily layer of the alcohol.

2. 1.0 cc. sec. octyl alcohol gave an opalescent solution with 1.2 cc. benzoate solution. 0.2 cc. H_2O caused cloudiness.

3. 1.0 cc. freshly distilled ethyl acetate were dissolved in 4.0 cc. benzoate solution by shaking. 2.0 cc. H_2O caused slight turbidity, 5.0 cc. H_2O however gave a clear solution.

4. 1.0 cc. paraldehyde was almost dissolved by 7.0 cc. benzoate solution. 2.0 cc. H_2O produced a crystal-clear solution which could be diluted with more water at will.

5. 1.0 cc. heptane dissolved in 10.0 cc. benzoate solution to a green-blue iridescent liquid; 1.0 cc. H_2O caused a heavy discharge of oil.

6. 2.0 cc. citronellol were dissolved in 2.0 cc. benzoate. 0.2 cc. H_2O caused cloudiness.

7. 1.0 cc. geraniol was dissolved by 4.0 cc. benzoate solution. 0.2 cc. H_2O caused cloudiness, more H_2O caused discharge of oil.

8. 0.5 cc. benzaldehyde dissolved on slight warming in 5.0 cc. benzoate solution. 5.0 cc. H_2O on warming caused separation of oily benzaldehyde.

9. 0.5 cc. cinnamaldehyde were dissolved in 7.0 cc. benzoate solution. H_2O discharged oily aldehyde immediately—whether in cold or on heating—.

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[1]) W. 47586, Kl. 12o, dated 29. 2. 1916. — [2]) Semmler, *Die ätherischen Öle*, vol. 3, p. 511. — [3]) *Pharm. Ztg.* 37 (1892), 180. Cf. *Pharm. Zentralh.* 33 (1892), 199; 40 (1899), 698; 43 (1902), 225. — [4]) *Bull. Acad. roy. Belgique* 35 (1897), 15. As per *Chem. Zentralbl.* 1898, I. 892. Cf. *Pharm. Zentralh.* 41 (1900), 126. — [5]) *Annal. de Pharm.* 1899, 348, 377 and 500. Cf. *Report* October 1899, 58. — [6]) *Chem. Ztg. Rep.* 25 (1901), 20. — [7]) *Pharm. Zentralh.* 42 (1901), 792; 51 (1910), 615. — [8]) *Biochem. Zeitschr.* 76 (1916), 107.

10. 0.5 cc. diethylketone dissolved in 4.0 cc. benzoate solution. H_2O can be added to this mixture at will.

11. 2.0 cc. benzyl alcohol dissolved in 0.5 cc. benzoate solution. 0.5 cc. H_2O caused cloudiness; 0.5 cc. benzoate solution cleared this again, and then 0.5 cc. more H_2O was tolerated.

12. 1.0 cc. phenylethyl alcohol gave a clear solution with 0.5 cc. benzoate solution. 0.2 cc. H_2O were tolerated, 0.5 cc. H_2O caused cloudiness.

13. 2.0 cc. cinnamic alcohol (liquefied) gave a clear solution with 1.0 cc. benzoate solution. 0.5 cc. H_2O caused cloudiness, addition of 1.0 cc. benzoate solution cleared the mixture again.

14. 2.0 cc. eugenol were dissolved in 2.0 cc. benzoate solution. 0.5 cc. H_2O caused cloudiness. More water precipitated oil.

15. 1.0 cc. cyclohexane (Kahlbaum) gave a clear solution in 1.0 cc. benzoate solution. The solution tolerated 1.0 cc. H_2O.

An investigation by H. Zeehuisen treats of the electrification by spraying *(Verstäubung)* of perfumes, and of intensity[1]) of odour. Only substances that are to some extent soluble in water take up a charge. 24 different perfumes, chosen arbitrarily, showed that in homologous series, odour and charge are parallel properties. The limits of perceptibility of odour and of charge are in general the same. Probably both intensity of odour, and electric charge depend on the volatility of the substance, as well as on the lowering of the surface-tension of water which it brings about.

A new method for the continuous measurement of light intensity with the "Graukeilphotometer" (grey wedge photometer) is described by W. Hecht[2]). The process is an improvement of the "Skalenphotometer" (scale photometer) introduced by Kissling[3]). The paper scale, rising in steps, is replaced by a continuous neutral grey wedge, thus increasing the possible time of exposure to light and lessening the limits of error. Hecht gives in his work an historical survey of the usual methods of light measurement hitherto used in botany. Whilst the "Normalfarbenphotometer" (normal colour photometer) is best for absolute measurements, the "Graukeilphotometer" best meets the demands for comparative light measurements, since measurements can be made simultaneously at a number of points, and for various times of exposure. The "Graukeilphotometer" deserves this much notice, since light measurements are of great importance in all departments of science, arts, and industry, and especially in plant cultivation.

Constitution and optical rotatory power of optically active substances. — H. Rupe[4]) has shown that in homologous series the characteristic wave lengths remain approximately constant. If they are displaced by more than 10—15 $\mu\mu$ by insertion of a group or by change in the linkings, we suspect relative or total anomalous dispersion. Previous researches have shown that the phenomena of anomalous dispersion can be traced to the increase of negative groups, and to the disturbing influence of multiple bonds, in which case the proximity of certain groups has an important influence. The normal rotation dispersion of organic substances is calculated from $\alpha_n = \frac{k_o}{\lambda_n^2 - \lambda_o^2}$. For liquid

[1]) *Koninkl. Akad. van Wetensch. Amsterdam, Wisk. en Natk. Afd.* 28 (1919), 11. As per *Chem. Zentralbl.* 1920, I. 234. Cf. *Reports* 1917, 114; 1918, 95. — [2]) *Sitzungsber. d. akad. Wiss. in Wien. Math.-naturw. Klasse Abt. IIa,* 127 (1918), No. 10. — [3]) Kissling, *Einfluss der Chemischen Lichtintensität auf die Vegetation.* 1895. — [4]) Cf. *Report* 1918, 96.

optically active bodies the following proposition is valid: — A body which when pure (in itself) shows normal dispersion, will likewise show normal dispersion when dissolved in an indifferent medium, and vice versa.

Later Rupe and Akermann[1]) came to the opinion that for anomalous dispersion, strong displacement of the characteristic wave lengths was necessary, but not sufficient.

In order to estimate the connection between constitution and optical rotatory power, it is essential to know the rotation dispersion as accurately as possible. It has already been shown that a change in constitution produces a change in the form and position of the dispersion curve. Further it is known that the solvent has a great effect on the rotation dispersion of dissolved substances. No definite rule as to the action of the solvent can be formulated at present. In the case of the methylene camphor series and its derivatives, with one exception, the rotation is always smaller when the compound is investigated in benzene solution. On the other hand the menthol derivatives when in solution show sometimes greater, sometimes less rotation.

The following relations between constitution and optical activity are known: If the properties of the asymmetric complex are not altered by chemical change, the parent substance and its derivatives have ions with the same vibration periods, or in other words λ_o^2 will be constant. For the activity coefficient k_m the rule holds that it is not altered by the number of groups in the molecule. k_m depends chiefly on the position of the atoms in space and on their mutual distances. If a compound has normal rotation dispersion and normal activity coefficient, there is a definite relation between the distances of the various groups and the molecular diameter (or molecular volume). If by some change in the molecule this relationship is disturbed, the activity coefficient also is altered.

Since the former measurements of the optical activity of the menthyl esters of keto acids must be now considered as imperfect, Rupe and H. Kägi[2]) have undertaken the study of the dispersion ratio of such esters for at least four colours. They have found that with the exception of acetoacetic ester, the influence of the solvent on the form of the dispersion ratio curve of the esters examined, is not important; on the other hand, the magnitude of the specific rotation is differently influenced by benzene. From acetosuccinic acid three menthyl esters can be prepared, whose rotatory power is in good accord with their constitutional formulæ. Via introduction of the diphenylmethane residue in the menthyl ester of acetoacetic acid, the $(d+l)$ und $(l+l)$ form are formed. The $(d+l)$ form shows a complex anomaly, the $(l+l)$ like the inactive acid disperses normally. In the synthesis of benzylacetoacetic ester the strongly lævorotatory $(l+l)$ form ($[\alpha]_D = -121.21°$) can be obtained together with a form of low melting point, which is considered to be a mixture of equal amounts of $(l+l)$ and $(d+l)$ form. In the phenylbenzoylacetic ester, keto and enolic forms can be detected. In benzene solution both have strong complex anomaly of the rotation dispersion. Benzal compounds (benzalacetoacetic ester, benzalbenzoylacetic ester, benzalpyroracemic ester) show great irregularity in the complex anomaly of rotation dispersion in benzene solution.

On the basis of the latest reports, Rupe adduces the following four classes of anomalous rotation dispersion of optically active organic bodies. (1) Total anomaly of a mixture of two substances with different sign of rotation (Biot). (2) Total anomaly of a compound which contains two asymmetric complexes, one lævo- the other dextro-

[1]) *Liebig's Annalen* 420 (1920), 1. — [2]) *Ibidem* 33.

rotatory. (3) The rotation dispersion curve has neither a maximum, a minimum, nor approaches a limiting value, but λ_α and λ_o^2 differ greatly from the normal values. (4) Apparent normal course of the curve $\frac{1}{[\alpha]}$ against λ^2 gives a straight line, but λ_α and λ_o^2 differ greatly from the usual normal value for the type of compound. (Relative anomaly.)

The methods of preparation and constants of the following compounds are given in the experimental part of the paper: — menthyl ester of diethylacetic acid, menthyl ester of *iso*propylacetoacetic acid, ethyl ester of diphenylmethylacetoacetic acid, menthyl ester of diphenylmethylacetoacetic acid, menthyl ester of benzylacetoacetic acid, menthyl ester of acetylacetoacetic acid, menthyl ester of benzoylacetic acid, menthyl ester of dibenzoylacetic acid, monomenthyl ester of acetosuccinic acid (α- and β-forms). By the action of menthol on the diethyl ester of acetosuccinic acid, a mixture of the above α- and β-forms is obtained.

With regard to the *optical refraction* of the resins, only isolated determinations had been made up to recent times. These were of very little use for practical purposes, since the methods used in the determinations were not given. That the refractive indices alone, and still more in connection with other physical properties, can be a valuable aid in the determination of resins of unknown origin has been shown by I. Greger[1]). Since neither the comparison methods by means of the polarisation microscope, nor the prism methods with the Fuess goniometer satisfied his needs, Greger determined the refractive indices by means of a Zeiss crystal refractometer. As comparison liquid he used Thoulet's solution (potassium-and-mercury-iodide solution) of refractive index 1.71813, and as source of light the sodium flame. Special methods were adopted to suppress as far as possible the volatilisation of impurities which affected the determinations. The refractive index of the resins can be derived approximately from their melting points.

Greger obtained the following results: — An index less than 1.530 is given only by Mexican elemi, and Brazilian copal from *Hymenæa Courbaril;* between n 1.530 and 1.550 lie copals, elemi, benzoin, pine resins, gum lac, Umiri resin, olibanum, sandarak, dammar; between n 1.550 and 1.60 lie pine resins, Chios mastix, Manila and Protium elemi, as well as certain copals; above 1.60 lie gamboge, Guajac resin, *Xanthorrhœa* resin, and dragon's blood. The refractive index is directly related to the melting point, hardness, density, and solubility when these are determined under equivalent conditions. On account of these physical constants the chemical investigation of the resins can be kept within narrow limits.

Botanical Notes.

A work by O. von Kirchner[2]) gives a list of the diseases of our medicinal and spice-plants caused by fungi. The diseases named 'leaf spot diseases' occur very frequently, and are caused by the fungi of the pyrenomycetes genus *Sphærella* and their closely related fruit-forms of the genus *Septoria, Ascochyta,* and others. Dull-brown or brighter spots with dark border are noticed on the leaves. They may spread to the stalks, and are here replaced by fungi of the genus *Phoma.* The rust-diseases, which appear on the stalks and leaves, may be recognised by pustules or little cushion-

[1]) *Sitzungsb. d. Akad. d. Wiss. in Wien. Math.-naturw. Kl., Abt. I,* 128 (1919). According to kindly forwarded reprint. — [2]) *Heil- und Gewürzpfl.* 3 (1920), 153.

like spots, from which a rust-coloured, brown or blackish powder often bursts. The rust is caused by rust fungi from the families *Puccinia, Uromyces* and others. Mildew fungi of the family *Erysiphe* cause the mildew diseases, where a white or bright grey dusty covering appears on leaves and stalks. Pale spots (so-called false mildew) on the leaves, on whose under-sides a coating of white or grey mold (mildew) appears, come from various members of the families *Peronospora* and *Plasmopara.*

The following diseases have been observed on our aromatic plants of high significance for our industry:—

Anethum graveolens, L., Dill:—Leaf spots caused by *Ascochyta anethicola,* Sacc.; stalk-spots caused by *Phoma Anethi,* Sacc.; rust caused by *Puccinia Petroselini,* Lindr.

Anthemis nobilis, L., Roman chamomile:—White rust (mold), caused by *Cystopus Tragopogonis,* Schröt.; false mildew caused by *Peronospora leptosperma,* DBy.

Archangelica officinalis, Hffm., Angelica:—Leaf-spots caused by *Phyllachora Angelicæ,* Fuck.; mildew caused by *Erysiphe umbelliferarum,* DBy.; false mildew caused by *Plasmopara nivea,* Schröt.; rust caused by *Puccinia Angelicæ,* Fuck.

Artemisia Absinthium, L., Wormwood:—Leaf spots caused by *Cercospora Absinthii,* Sacc. and *C. olivacea,* Otth; rust caused by *Puccinia Tanaceti,* DC.

Artemisia Dracunculus, L., Tarragon:—Rust caused by *Puccinia Tanaceti,* DC. and *Aecidium Dracunculi,* Thüm.

Carum Carvi, L., Caraway:—False mildew caused by *Plasmopara nivea,* Schröt.; yellowing and withering of the leaves after previous appearance of stroke-shaped weals, caused by *Protomyces mascrosporous,* Ung.; dying-off of the stalks on appearance of hard black fungus bodies, caused by *Sclerotinia Libertiana,* Fuck.

Coriandrum sativum, L., Coriander:—Nothing known.

Fœniculum vulgare, Mill., Fennel:—Stalk spots caused by *Phoma fœniculacea,* Sacc.; false midlew, caused by *Plasmopara nivea,* Schröt.; dying-off of the whole plant with the appearance of hard black fungoid bodies on and in the stalk, caused by *Sclerotinia Libertiana,* Fuck.; dying-off of the roots, which are covered with a dark violet fungoid web, caused by *Rhizoctonia violacea,* Tul.

Inula helenium, L., Elecampane:—Mildew caused by *Erysiphe lamprocarva,* Lev.; rust caused by *Celeosporium Sonchi,* Lev.

Lavandula officinalis, Chaix., Lavender:—Leaf spots caused by *Septoria Lavandulæ,* Desm.

Levisticum officinale, Koch, Lovage:—Leaf spots caused by *Ramularia Levistici,* Oud., *R. Schröteri,* Syd. and *Septoria Levistici,* West.

Melissa officinalis, L., Balm mint:—Leaf spots caused by *Septoria Melissæ,* Desm.; rust caused by *Puccinia Menthæ,* Pers.

Mentha crispa, L., Spearmint:—Rust caused by *Puccinia Menthæ,* Pers.; mildew caused by *Erysiphe Galeopsidis,* Db.

Mentha piperita, L., Peppermint:—Rust caused by *Puccinia Menthæ,* Pers.; leaf-spots caused by *Phyllosticta decidua,* Ell. and Kell.; mildew caused by *Erysiphe Galeopsidis,* DC.

Origanum Majorana, L., Marjoram:—Rust caused by *Puccinia Menthæ,* Pers.

Petroselinum sativum, Hffm., parsley:—Leaf spots caused by *Septoria Petroselini,* Desm. and *Cercospora Apii,* Fres.; stalk-spots caused by *Phoma Anethi,* Sacc.; false mildew caused by *Plasmopara nivea,* Schröt.; rust caused by *Puccinia Petroselini,* Landr.; dying-off of whole plant on appearance of hard black fungoid bodies caused by *Sclerotinia Libertiana,* Fuck.; dying-off of roots, which are covered with a deep-violet fungoid web, caused by *Rhizoctonia violacea,* Tul.

Pimpinella Anisum, L., Aniseed: — mildew caused by *Plasmopara nivea*, Schröt.; rust caused by *Puccinia Pimpinellæ*, Mart.

Ruta graveolens, L., Rue: — leaf-spots caused by *Sphærella Rhea*, Fautr.

Salvia officinalis, L., Sage: — leaf-spots caused by *Ascochyta vicina*, Sacc.; stalk-spots caused by *Phoma Salviæ*, Brun.; mildew caused by *Oidium erysiphoides*, Fr.

Satureja hortensis, L., Summer Savory: — Rust caused by *Puccinia Menthæ*, Pers.

Sinapis alba, L., White mustard, and *Sinapis nigra*, L., black mustard: — Leaf-spots caused by *Septoria Brassicæ*, Ell. and Ev.; false mildew caused by *Peronospora parasitica*, Tul.; white rust caused by *Cystopus candidus*, DBy.; falling and rotting of the seedlings, caused by *Pythium Debaryanum*, Hesse; excrescences on roots caused by *Plasmodiophora Brassicæ*, Wor.

Thymus vulgaris, L., Thyme: — Rust caused by *Puccinia Menthæ*, Pers.

Valeriana officinalis, L., Valerian: — Leaf-spots caused by *Ramularia Valerianæ*, Sacc.; mildew caused by *Erysiphe communis*, Fr.; false mildew caused by *Peronospora Valerianæ*, Trail; rust caused by *Uromyces Valerianæ*, Fuck.

The few means with which the above-mentioned diseases can be combated (blue vitriol and lime liquor, and similar liquids) lessen the value of the crop, so far as flowers, leaves, and stalks are concerned; and therefore their use is self-prohibitory. The only way left is to increase the resisting powers of the cultivated plants against diseases. This can occur, when races or individual plants of greater resisting powers — or possessing complete immunity wherever possible — are raised, and their powers of resistance increased by suitable methods of culture. A thorough discussion of this question of plant raising is found in the original work to which reference is now made.

Phytophysiological Notes.

Since the literary information on the amygdalin content of bitter almonds is very contradictory, L. Rosenthaler has carried out a large series of amygdalin estimations on four various kinds of almonds[1]). He found the hydrocyanic acid present in the almonds, from which he calculated the amygdalin content. It turned out that even in the same samples, which came in part from chemists and druggists, the amygdalin content varied. The contents in the medium quality amounted to: 4.29 per cent., 4.28 per cent., 3.43 per cent., 3.25 per cent.; those of the lowest quality: 2.50 per cent., 2.14 per cent., 0.25 per cent., 2.09 per cent.; those of the best quality: 6.90 per cent., 8.48 per cent., 5.25 per cent., 4.50 per cent. With the three kinds the lightest almonds were richer in amygdalin than the heaviest; with the fourth kind, it was just the opposite. The customary rule, that small almonds contain most amygdalin is valid, but not without exceptions.

Rosenthaler[2]) has also endeavoured to answer the much-raised question, in which form hydrocyanic acid occurs in the vegetable kingdom. From his own investigations and information obtained from literature, he arrives at the result, that hydrocyanic acid is found in plants in the combined form mostly as glucosides. Only in the combined form, as the hydroxy nitrile glucoside, does the acid occur in bitter almonds, cherry laurel leaves, linseed germs, peach leaves, the seeds of *Phaseolus lunatus*, L. and in *Sorghum vulgare*, Pers. The small amount of hydrocyanic acid which has been found in the buds of *Prunus Laurocerasus*, L., and in the leaves of *Sambucus nigra*, L., is not combined with glucosides.

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[1]) *Berichte d. deutsch. pharm. Ges.* 30 (1920), 13. — [2]) *Schweiz. Wochenschr. f. Chem. u. Pharm.* 57 (1919), 571.

The question, whether the hydrocyanic acid was present in the free state from the commencement, or whether it first existed as hydroxynitrile could not be decided. Yet it does not seem impossible that traces of hydrocyanic acid occasionally occur.

Physiological and Pharmacological Notes.

A work of L. Ruzicka[1]) deals with the principles of the chemistry of smell in which the author sets down a new theory of smell reactions. In the investigation of the relations between the constitution and effects of chemical compounds on the individual sense organs the greatest successes were obtained in colour chemistry. The reason for this lies in the fact that the colours, independently of the sense of sight, can be classified into a strictly established scientific system. In smell and taste, on the contrary, chemical reactions take place in the human body itself, and the influence of the central nervous system must be taken into account. Under these conditions it is difficult to obtain objective results. Hence all attempts to establish a system of smells were deficient. Henning's system of smell[2]) also is incorrect, for smells cannot be classified according to chemical principles. Ionone belongs to the same chemical class of smell of Henning as tetrahydroionone, but on account of its violet odour must be placed in a different psychological class of smell than the cedar-like smelling tetrahydroionone.

From the point of view, that smell arises from a chemical reaction in the nose, Ruzicka defines as scent (perfume), a body which is soluble in the air and chemically reacts with substances in the olfactory mucous membrane, which reaction excites the olfactory nerve. Formerly the chemical radicles characteristic of scents, as OH, CHO, CO, COOR, and others, were denoted as osmophoric groups[3]). Analogous to the Ehrlich method of expression, Ruzicka calls the substances of the olfactory mucous membrane, through which the scents are fixed "osmoceptors". The perfume molecules entering the nose combine with those (primary) osmoceptors most capable of reacting with them, through which a certain smell is then called forth. If these osmoceptors are present in sufficient quantity, or rapidly enough reformed by the organism, then the smell remains constant. On the other hand, if the osmophoric group of the perfume, after the consumption of all primary osmoceptors enters into reaction with other (secondary) osmoceptors, then another smell can come into being,— that is, there is a sudden change of smell.

When a perfume in concentrated form is applied, then the primary osmoceptors may be quickly neutralised, or both osmoceptors may react simultaneously. Then the first smell will be partly or completely covered by the second. The variation of smell in concentrated and diluted conditions of many perfumes rests on this fact, as in the case of indole, which when concentrated has a fæcal odour, but when diluted has a pleasant smell. If the osmophore group reacts only with one osmoceptor, then after saturation of the primary osmoceptors loss of smell supervenes. An example of this is given by the weak smell of concentrated violet perfume, and the rapid dulling of the organ of smell, when the same perfume in a diluted state is present. By assuming that occasionally, no chemical reaction can take place in the mucous membrane of the nose, then the fatigue symptoms of the organ of smell may be explained. Often an organ of smell blunted for one substance (vanillin), is yet sensitive to another (coumarin); in this case the two bodies have different osmophoric groups and can be combined with different osmoceptors.

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[1]) *Chem. Ztg.* 44 (1920), 93, 129. — [2]) Cf. *Report* 1917, 124. — [3]) *Ibidem* 129.

The constitution of the perfume is the most important thing for the kind of smell. In the reaction of the osmophoric group with various osmoceptors only the finer dulling of the smell is caused, as a rule. There is hardly a chemical characteristic existing, whose influence on the sense of smell is always approximately the same. In symmetrical trinitrotoluene the smell of musk first appears, when an additional alkyl is joined on to the molecule. Likewise with the ionone perfumes two methyl groups at least are necessary for producing the smell of violets, which only becomes distinctly noticeable when three methyl groups are added. Phthalide also is odourless, and only with *iso*butyl-phthalide is the celery odour obtained. In this connection however, perfumes are also known (vanillin and coumarin) which are built similarly to the above, in which however, the entrance of alkyl groups is of no significence, or even damaging for the odour.

A universal rule on the relations between smell and constitution of chemical compounds cannot on this account be further set down, since the influences of the central nervous system on the results of investigation, and the reactions taking place within the human body, give various individual results. Only uncertain information can be indirectly obtained as regards the question, "with which compound in the organism do the effective odoriferous substances react?" since it is a case of unweighable quantities with perfumes.

In connection with this work of Ruzicka, reference may be made to the remarks, which the theory of Teudt[1]) on the origin of smell, has caused many authors[2]) to make. Amongst other things T. H. Durrans observes that Teudt does not appear to know the works of the physiologists Zwaardemaker and Backman[3]). Further it is not proved that the molecules of the perfume would be altered in no way through the streaming ont of the odour. Facts like the fatigue phenomena and Kremer's[4]) experiments on the absorption of perfumes in lipoid-containing water spoke against the assumption of Teudt. Teudt's theory also cannot be brought into agreement with the law of the conservation of energy.

In a similar manner Parry raises several objections against these phantastic speculations, and emphasises that the smell of a body is a property which also depends on the person who smells, and cannot be treated as an objective phenomenon.

Smell and Chemical Constitution.—Referring to an earlier work on Smell and Chemical Constitution[5]), T. H. Durrans[6]), in a controversy with E. J. Parry, emphasises that between the smell and volatility of a substance there exists no fundamental connection. According to Zwaardemakers proofs[7]), odour strength is independent of the vapour-forming phase, but depends on the solubility of the substance in the nose-fluid.

Neither does the quantity of perfume present—so long as it is not insufficient—alter the odoriferous power. What one really smells, is a solution in air of the vapeur-forming body; and the strength of the solution is dependent on the vapour pressure and not on the amount of substance present.

Further Durrans mentions his theory on smell and free partial valencies. In cases where one molecule attracts the other, there are no free partial valencies at hand; and no smell arises. Sodium acetate is odourless, since the partial valencies are completely bound or, according to the Woker conception, since sodium is positive

[1]) Cf. *Report* **1919**, 104. — [2]) *Perfum. Record* **11** (1920), 12. — [3]) Cf. *Reports* Oct. **1904**, 104; **1917**, 117. — [4]) Cf. *Report* **1918**, 112. — [5]) Cf. *Report* **1919**, 107. — [6]) *Perfum. Record* **10** (1919), 266. — [7]) Cf. *Report* October **1904**, 104.

and the CH_3COO residue is negative. The halogens chlorine, bromine, and iodine on the contrary, which have free partial valencies, smell strongly.

Likewise in relation with an earlier work[1]) on smell and chemical constitution, stands the list of odoriferous substances, which Durrans[2]) published. In the compilation the most important compounds which are characterised by their smell — aliphatic and aromatic hydrocarbons and aliphatic alcohols were placed in classes, with the elements carbon, hydrogen or oxygen noted. The odour-power was seldom mentioned; the kind of smell very indefinitely described, *e. g.*, *n*-octane, weak ethereal; *n*-nonane, mild, sweet; *p*-ethyl-butylbenzene, weak, like carrots.

An apparatus for carrying out smell measurements, constructed a few years ago by M. Fournie, is recommended in a French periodical[3]). The olfactometer consists of two test-tubes, one of which can be pushed into the other; one is pierced with a row of vertical holes, the other with a row of holes of a spiral form. By twisting the glasses — in the interspace of which the odorous body is placed — the various holes can be open or closed at will. Since a clearly understandable description is not at hand, we must content ourselves with this information.

Under the title *"On the Bees' Sense of Smell, and its Significance in Flower-Biology"*[4]) K. von Frisch has published his interesting researches in book form. These researches were thoroughly discussed by us in the *Report* of **1919**, p. 108.

Like Frisch[5]), F. Knoll[6]) arrived at similar results in his investigations, by which he wanted to ascertain if it is possible to train insects for recognizing colours. The experiments showed that with the exceptions of red and green, colours were perceived by bees at a much greater distance than they perceived smells. Bees accustomed to the yellow helianthemum flowers (yellow rock rose) were only attracted by the colour, and flew just as often also to the yellow flowers of other plants growing near, up to a distance of 1 to 0.5 cm. Then at last, recognising their error, they flew on to the next yellow flower, on which they alighted, in case it might be a *Helianthemum*. A contrary example to this was furnished by those bees which collected honey from the blue to red-violet flowers of *Echium vulgare* and at the same time flew to the blue- to purple-coloured flowers of *Delphinium*, *Cichorium*, *Campanula*, *Clematis Viticella*, L., *Vicia dasycarpa*, Tenore, and *Salvia officinalis*, L. They did not take pollen from these flowers.

From these and other investigations it further resulted that the universal honey perfume so often mentioned in biological books, plays no part worthy of mention. It is always a case of the specific odour of the flowers in question, which is only perceived by the insects in the immediate neighbourhood, and only then attracts them.

In order to completely eliminate the action at a distance of the smell of the flowers, Knoll caused the bees to approach them in a direction perpendicular to a current of air passing over and in contact with the flowers. In other cases the flowers were surrounded by little glass tubes. All experiments led to the result that a colour attraction is possible with certain insects, but that red or green had no influence.

Investigation and Valuation of Scent-stuffs for Commercial Purposes: — Attempts have often been made with the help of special apparatus (olfactometer) to estimate the intensity of smell as sense stimulant. We have discussed Zwaardemaker's and Henning's

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[1]) Cf. *Report* **1919**, 107. — [2]) *Perfum. Record* **11** (1920), 79. — [3]) *La Parfumerie moderne* **11** (1918), 143. — [4]) Jena **1919**. Publishing House of G. Fischer. — [5]) Cf. *Report* **1919**, 108. — [6]) *Die Naturwissenschaften*, **1919**. No. 24. According to kindly forwarded reprint.

thorough treatment of this subject before[1]). V. C. Allison and S. H. Katz[2]) have recently published similar researches. These experiments were specially carried out to ascertain which smells might find application as danger signals in mining work[3]).

Allison and Katz made use of an apparatus called "Odorometer", in order to estimate the strengths of smells, and therewith the efficacy of the smell-stuff used. The apparatus was used as follows:—By means of an air pump, air was caused to flow uniformly through several current-meters, and a U-tube filled with the liquid containing the odoriferous body. The measured air saturated with the odour, was now mixed with a measured amount of pure air and then led into a funnel, into which the experimenter had to smell, for the purpose of determining the smelling power. The U-tube was weighed before and after the experiment, and from the difference, the amount of smell-stuff was calculated which had passed over in the air. From this the concentration of the smell-stuff in the air could be reckoned both by weight and by volume. After a single inspiration ("sniff"), the smell strength was assessed as follows by the person who had to carry out the whole of the experiments:—I perceptible; II weak; III fairly strong; IV strong; V very strong.

We reproduce here the most important of the 24 smell-stuffs investigated:—

Smell-stuff.	Smell-stuff in parts by volume in 1000000 parts by volume of air. Intensity of the smell.					Smell-stuff in milligrammes in 1 litre of air. Intensity of the smell.				
	I	II	III	IV	V	I	II	III	IV	V
Artificial musk	—	—	—	—	—	0.00004[4])	—	—	—	—
Iodoform	1.1	—	—	—	—	0.018[4])	—	—	—	—
Diamylsulphide	0.2	1	1.6	1.7	2.2	0.001	0.007	0.0115	0.012	0.015
Amylisovalerianate	1.7	3	6	10	12	0.012	0.018	0.039	0.072	0.082
Propylmercaptane	2	7	9	14	17	0.006	0.020	0.028	0.043	0.054
Butyric acid	2.4	6	18	91	161	0.009	0.021	0.066	0.329	0.580
Valerianic acid	7.0	29	125	332	962	0.029	0.119	0.523	1.394	4.036
Methyl salicylate	16.1	23	29	244[4])	—	0.100	0.145	0.179	1.526[4])	—
Peppermint oil	—	—	—	—	—	0.024	0.032	0.109	9.332	0 348
Ethyl acetate	190	339	615	1236	1753	0.686	1.124	2.219	4.457	6.733
Chloroform	674	1389	2600	5887	9528	3.300	6.800	12.733	28.833	46.666

It is seen from this table that:—

(1) With the same concentration of the smell-stuff in air, the intensity of the individual smells is very variable.

(2) Concentration and intensity of the various smell-stuffs show no relation to each other, that could be formulated into a law.

(3) Sleep-effecting stuffs have lesser smell intensities, probably on account of their benumbing influence on the olfactory nerves.

Physiological Effect of Essential Oils. — S. Furukawa has published a series of investigations on the connection between chemical constitution and physiological effect of essential oils. Since the original work was not to be procured, we can only reproduce the information from an abstract[5]). According to this, the alicyclic alcohols containing a CHOH group, their esters and the lower aldehydes have a cooling taste, aromatic hydrocarbons have a stimulating taste, and ketones a bitter taste[6]).

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[1]) Cf. *Reports* October **1904**, 104; **1917**, 123. — [2]) *Journ. ind. eng. Chem.* **11** (1919), 131. — [3]) In America odoriferous substances are already utilised for various industrial purposes. Thus the leaking of boilers and distributing tubes under high pressure, is made known by peppermint or wintergreen oil. — [4]) Maximum concentration available. — [5]) *Tokio Chem. Soc.* As per *Perfum. Record* **19** (1919), 200. — [6]) Cf. also *Reports* April **1907**, 114; October **1910**, 156; **1916**, 105; **1919**, 107.

In order to study the toxic and narcotic effects of perfumes[1]) a merlin (small river fish) was allowed to remain for 24 hours in perfume solutions of various concentrations. In homologous series the toxic effect decreased with the increase in molecular weight of the substance, but on the contrary the narcotic effect increased. The total physiological effect in general — the sum of the toxic and narcotic effects — is proportional to the molecular weight within a certain limit, beyond which the solubility in water or lipoids suddenly decreases.

To the many books recently published on the *antiseptic properties of essential oils*[2]) comes another by F. Bonnaure[3]) on the same subject. He brings forward something new, as he also studied the effect of vapour-forming substances on cultures of staphylococci. Staphylococci in bouillon were killed within an hour after the addition of terpene-free lavender and rosemary oils, but only after 4 hours on adding eucalyptole. Whilst the vapours from phenol, eucalyptole, terpineol, geraniol, lavender oil (château neuf), camphor-free lavender oil were still ineffective after 8 hours, vapours from terpene-free rosemary oil killed after 2 hours, and those of those of "standard" lavender oil, and of lavender oil terpenes killed the same bacteria after 5 hours.

I. R. Spinner[4]) has published an article on the *toxicology of eucalyptus oil and other essential oils*, in which he endeavours to further ascertain the causes of the poisonings brought about by the oils in question. It is easily possible that eucalyptus oil, that has given rise to symptoms of poisoning[5]) when taken in greater quantities, has been adulterated with products containing phellandrene, as oil of *Eucalyptus Amygdalina*, Labill., and similar eucalyptus species[6]). The eucalyptus oil used in medicine, which comes from *Eucalyptus Globulus*, Labill., contains 60 per cent. of eucalyptole at least, but no phellandrene. Since Erben reckons the phellandrene-containing fennel oil amongst the convulsion-producing substances, Spinner believes that the phellandrene in eucalyptus oil also can be the toxic ingredient. Physiological experiments with this terpene appearing often in nature[7]), have up to the present been only performed by Fromm and Hildebrandt[8]). The authors establish that the hydration of phellandrene[9]) to phellandrene glucuronic acid takes place in the body. Further, according to Spinner, the phenol tasmanol, found by Smith[10]) in several eucalyptus species (*E. linearis* and *E. Risdoni*), may have caused the poisonous properties of the oil in the cases mentioned.

The toxicological significance of the essential oils depends upon their camphor and terpene contents. Erben made the following classification:—

Convulsion-producing are: — Camphor and the oils of *Thuja orientalis*, L., *Thuja occidentalis*, L., *Tanacetum vulgare*, L., *Artemisia Absinthium*, L., *Salvia pratensis*. L., *Fœniculum vulgare*, L., *Rosmarinus officinalis*, L., *Matricaria Parthenium*, L., *Juniperus virginiana*. L., *J. Sabina*, L., *Mentha Pulegium*, L., *Hedeoma pulegioides* (L.), Pers., *Asarum europœum*. L., *Sassafras officinale*, Nees, *Apium Petroselinum*. L.

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[1]) Cf. also *Reports* October **1903**, 131; October **1907**, 125. — [2]) Cf. *Report* **1919**, 112. — [3]) *Parf. moderne* **12** (1919), 151, 152. — [4]) *Deutsche Med. Wochenschr.* **46** (1920), 389. — [5]) Cf. p. 34 of this *Report*. — [6]) Also the phellandrene-containing eucalyptus oils were exclusively obtained by distillation of the leaves, not by pressing, as Spinner appears to assume. — [7]) Spinner speaks only of phellandrene, without taking into account the various modifications. The *d*-α-phellandrene, occurring in bitter-fennel and elemi oil, and *l*-α-phellandrene present in the oil of *Eucalyptus Amygdalina* are to be sharply distinguished from the β-phellandrene of water-fennel oil. — [8]) *Zeitschr. f. physiol. Chem.* **33** (1901), 592; *Report* April **1902**, 84. — [9]) The various modifications of phellandrene were unknown at that time. — [10]) Cf. *Report* **1916**, 30.

Narcotic are: — Turpentine oil and the oils of *Pimpinella Anisum*, L., *Caryophyllus aromaticus*, L., *Ruta graveolens*, L., *Thymus vulgaris*, L., *Achillea millefolium*, L., *Eucalyptus Globulus*, Labill., *Myrtus communis*, L., *Laurus nobilis*, L., *Melaleuca Leucadendron*, L., *Valeriana officinalis*, L., *Matricaria Chamomilla*, L., *Anthemis nobilis*, L., *Ledum palustre*, L., *Juniperus communis*, L.

"Exitonarcotic" are Peru balsam and the oils of *Carum Carvi*, L., *Myristica fragrans*, Houtt., *Cinnamomum Cassia*, Blume, and *Toluifera Pereirœ*, Baill.

The representatives of the first group especially are most widely used as abortefacients, according to Spinner, and it is desirable to draw up a list of the constituents of the oil, to which the toxic effect is due. The thujone and the sabinol groups must be placed first. Thujone is the strongest and most widely spread of all poisons contained in essential oils, and is found in the thuja species, in wormwood, sage and tansy. The toxic effect of wormwood has long been known; it led to the absinthe prohibition in Switzerland and France. The use of tansy as a worm-remedy has also caused many cases of poisoning. Sabinol, the most effective constituent of savin oil, approaches thujone very closely in poisonous qualities; this widely spread abortefacient has quite similar deleterious effects as those of thujone-containing oils. Although these remedies are everywhere abused for purposes of abortion, most authors consider them of little worth for this purpose. Abortion in these cases is to be looked upon as a secondary effect of the general and severe damage done to the health.

The other groups — somewhat less poisonous — of the convulsion-producing oils are, that of the pulegone the myristicin group, the *iso*myristicin group, the apiole group, and the safrole group. All these compounds cause fatty degeneration of the parenchymatous organs, especially the liver. The myristicin-containing nutmeg, which in now used in its native place, Java, for the preparation of love potions and abortefacients just as the apiole freely sold by the chemists, are by no means harmless bodies, and have often caused death when taken in larger quantities than usual. Spinner also mentions that according to Zernik, myristicin is present in apiole capsules instead of parsley camphor. We may say that this fact is not surprising and easily explained, for according to Thoms[1]) French parsley oil consists for the most part of myristicin[2]).

According to J. Jacobson, cultures of the *Bacillus tuberculosis* were dissipated by *benzyl alcohol* and partly bleached. After the action of the alcohol the bacilli are less easily colored with carbolfuchsine (1 : 100). Benzyl alcohol liquefies the excretion, and causes, when subcutaneously injected in quantities of 0.02 g. into tuberculous guinea-pigs, no local or general reaction[3]) within a period of 10 days.

Benzylbenzoate has a sedative effect on spasms according to D. I. Macht[4]), especially on the involuntary muscles, less on the voluntary. In convulsive dysmenorrhœa, in intestinal and stomach spasms, in threatening miscarriage, in kidney- and gall stone colic, the ester has proved to be of service. Its efficacy as the blood-pressure reducing agent is more lasting than that of the nitrates. *Benzyl alcohol* is especially valuable as a local anæsthetic and in the treatment of venereal diseases. Both the remedies are only slightly poisonous.

A bibliography on the *effects of natural and artificial camphor* is to be found in the *Digest of Comments on the Pharmacopœia of the U. S. A. for* **1915**, 211.

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[1]) Cf. *Report* April **1904**, 67. — [2]) Formerly the French designated as apiole the alcoholic extract of parsley seeds, as well as apiole itself. — [3]) *Compt. rend. Soc. de biologie* **82** (1919), 1246. As per *Chem. Zentralbl.* **1920**, I. 537. — [4]) *Journ. Pharmacol. Proc.* **13** (1919), 509. As per *Chem. Abstracts* **14** (1920), 1387.

In experiments on the ears and hearts of rabbits N. P. Likhatcheva[1]) proved that *camphor, borneol* and *menthol* in diluted solutions of 1:2500 and 1:5000 enlarged the coronary and peripheral blood vessels.

Literary information on the *application of thymol and carvacrol* as remedies for hook-worms, pellagra and as antiseptics, is to be found in the *Digest of Comments on the Pharmacopœia of the U. S. A. for* **1915**, 428.

Since *carvacrol* (*iso*propyl-*o*-cresol) very closely resembles thymol (*iso*propyl-*m*-cresol) chemically, it was supposed that just like thymol[2]) it could find application as a worm remedy. It appears from S. T. Darling's experiments on dogs, that the relative efficacy of carvacrol as compared with that of chenopodium oil amounts to only 36 per cent. In addition carvacrol has very unpleasant and dangerous secondary effects on the mucous membrane, so that its use as a worm remedy is out of the question[3]).

The *thymol ester of palmitic acid* is recommended by Munk[4]) as a good remedy for trichinosis. According to him, the increase of certain forms of the white corpuscles (eosinophily) is an early diagnostic sign of this disease. At this stage the trichinæ can be completely expelled by the ester, so long as they are yet in the intestinal canal.

The ethyl ester of cinnamic acid. — This ester is named as an agent for the differential diagnosis between the dysentery bacteria of types Flexner and Hiss. In the presence of 0.025 g. ester in 10 cc. culture liquid, only the cultures of Flexner's dysentery bacteria develop, whilst the bacteria of the type Hiss and Shiga do not grow in it[5]).

On poisoning symptoms due to taking *eucalyptus oil,* see p. 34 of this *Report.*

On experiments on dogs with *methyl salicylate,* see p. 58 of this *Report.*

On the *application of mustard oil as a skin irritant,* see p. 42 of this *Report.*

On the *use of turpentine oil in urinary diseases,* see p. 58 of this *Report.*

Chemical Notes.

In connection with earlier works on *condensation of formaldehyde with several unsaturated compounds*[6]) H. I. Prins found that the aqueous and acetic acid solutions of sulphuric acid and formaldehyde behave differently with the substances coming under consideration[7]). Styrene, camphene and cedrene either do not react, or react very slowly with aqueous sulphuric acid solution of formaldehyde; anisole and *iso*safrole react readily, safrole, on the contrary, does not react. It can be assumed that by the addition of CO to C:C a four-ring is formed, which either on taking up water, changes into 1,3-glycol, $H_2C{\cdot}OH(RH)C{\cdot}CH{\cdot}OH{\cdot}R$, or on taking up formaldehyde forms a methylene ether $\begin{matrix} R{\cdot}HC{\cdot}O{\cdot}CH_2 \\ | \quad\quad > O \\ R{\cdot}HC{\cdot}H_2C \end{matrix}$, or is converted into an unsaturated primary alcohol.

From styrene, dissolved in glacial acetic acid with 10 per cent. sulphuric acid, and trioxymethylene, at a temperature below 40°, the methylene ether of the 2-phenylpropyl-

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[1]) *Russkij Wratch* No. 15, **1916**. As per *Digest of Comments on the Pharmacopœia of the U. S. A. for* **1916**, 225. — [2]) Cf. *Report* **1919**, 75. — [3]) *Bull. Imp. Inst.* **17** (1919), 426. — [4]) *Pharm. Ztg.* **65** (1920), 416. — [5]) *Compt. rend. Soc. de biologie* **82** (1919), 726. As per *Chem. Zentralbl.* **1919**, III. 827. — [6]) Cf. *Report* **1918**, 124. — [7]) *Koninkl. Akad. van Wetensch. Amsterdam, Wisk. en Natk. Afd.* **27** (1919), 1496. As per *Chem. Zentralbl.* **1919**, III. 1001.

glycol-1,3[1]) was obtained, a colorless oil (b. p. 128 to 130°, 13 mm; $d_{4^\circ}^{20^\circ}$ 1.1111; n_{D18° 1.5306; mol. refract. 45.64); further 2-phenylpropylglycol-1,3 was obtained, a colorless viscous liquid (b. p. 176°, 13 mm.; $d_{4^\circ}^{19^\circ}$ 1.1161; n_{D19° 1.5427; mol. refrac. 42.92), which quantitatively passed over into a diacetate (b. p. 162 to 164°, 13 mm.). Anethole yielded, after three days' stirring with formaldehyde in 30 per cent. sulphuric acid, the methylene of the *p*-methoxyphenylbutylglycol, a colorless, viscid fluid (b. p. 168 to 170°, 13 mm.; $d_{4^\circ}^{16^\circ}$ 1.1197; n_{D16° 1.5344; mol. refrac. 57.78). On oxidising the methylene ether with potassium permanganate anisic acid was produced. It is to be concluded from this, that the nucleus is not attacked by the formaldehyde. *Iso*safrole treated analogously with formaldehyde gave the methylene ether of the 3,4-methylenedioxyphenylbutylglycol, a colorless, viscid fluid (b. p. 182 to 184°, 13 mm.; $d_{4^\circ}^{17^\circ}$ 1.2272; n_{D17° 1.5408; mol. refract. 56.84). Camphene was boiled under a reflux condenser for 3 days with trioxymethylene in glacial acetic acid. The oil was separated with water, dried, and on boiling with glacial acetic acid was converted into homocamphenol acetate (b. p. 124 to 128°, 13 mm.; $d_{4^\circ}^{19^\circ}$ 1.0013; n_{D19° 1.4821; mol. refract. 59.23). On boiling pinene with trioxymethylene and glacial acetic acid, saponifying and fractionating, the colorless homopineol was obtained (b. p. 113 to 116°, 13 mm.; $d_{4^\circ}^{19^\circ}$ 0.9720; n_{D19° 1.4862; mol. refract. 49.05). In a similar way limonene with formaldehyde gave the colorless homolimonenol (b. p. 122 to 126°, 13 mm.; $d_{4^\circ}^{19^\circ}$ 0.9757; n_{D19° 1.5026; mol. refract. 50.26). Cedrene, after 3 days' stirring with formaldehyde in glacial acetic acid and 10 per cent. sulphuric acid, gave, after saponifying, in addition to many higher boiling point products, the homocedrenol, a colorless, viscid liquid (b. p. 168 to 171°, 13 mm.; $d_{4^\circ}^{19^\circ}$ 1.0270; n_{D19° 1.5183; mol. refract. 69.08).

The method of *moist chlorination*, which is especially advantageous with low-boiling *hydrocarbons*, has already been employed by O. Aschan[2]) on already substituted hydrocarbons, *e. g.*, ethyl chloride, *iso*amyl chloride, ethylene chloride, chloroform, propyl bromide, ethylene bromide, ethyl iodide, toluene and xylene. Here the presence of water acts catalytically in the forming of a hydrate $\begin{matrix} H \\ H \end{matrix}\!\!>\!O\!<\!\!\begin{matrix} Cl \\ Cl \end{matrix} + n\,H_2O$, which indeed, only below 0° really separates out, but which, however, also at higher temperatures can temporarily exist. The catalytic effect of light rests probably on the formation of the complex Cl_3 in the chlorine exposed to day light.

We take the following announcement on anethole from a work on the *catalytic effect at solid surfaces* and on the *reduction of substances with ethylene linkages* by E. F. Armstrong and T. P. Hilditch[3]). On the reduction of this ether in presence of 0.15 per cent. of nickel at 180° a solid crystalline body was produced — still to be investigated — together with the normal product of reaction, dihydroanethole, preferably by working with sealed apparatus.

Re *allyl compounds* see p. 41 of this *Report*.

Hydrocarbons.

Analysis of hydrocarbons with the aid of bacteria. — Up to now it has been impossible to isolate cyclic saturated hydrocarbons from mixtures with aliphatic saturated hydrocarbons, as they come into question with the petroleums. These two series of

[1]) The position of the phenyl groups is not apparent from the formula. — [2]) *Finska Kemistsamfundets Meddelanden*. As per *Chem. Zentralbl.* **1919**, I. 221. — [3]) *Journ. Soc. chem. Ind.* **39** (1920), T. 122.

hydrocarbons are so similar to one another in their chemical behaviour that the paraffins cannot be attacked without the simultaneous destruction of the naphthenes. Only a biochemical process could promise success, and after several failures J. Tausz and M. Peter[1]) succeeded in this way. Many biochemical methods have up to now been utilised (decomposition of racemates and various sugars by micro-organisms) in chemistry, but never in the analysis of hydrocarbons. Hydrocarbons, especially petroleum and its products, have for long enough been regarded as strong bacteria poisons. They were therefore introduced into medicine as good disinfection agents and as remedies. Then Tausz for the first time observed in 1911, when he was examining Wels bitumen, that also raw petroleum oils could serve as carbon and energy sources for bacteria and fungi. Later it was found that benzene, toluene, xylene, paraffin, benzine, petroleum, and paraffin oil could be assimilated by various species of microbes.

Tausz now was able to isolate three new hydrocarbon bacteria from garden-soil, which he named *Bacterium aliphaticum*, *B. aliphaticum liquefaciens*, and paraffin bacterium. The occurrence of these bacteria in garden-soil is probably connected with the wide dissemination of the hydrocarbons in the mineral, vegetable and animal kingdom.

B. aliphaticum were obtained by treating an inorganic or organic nutrient solution with a few drops of *n*-hexane, and infecting it with various samples of garden earth. The specific exciters of the hexane decomposition were formed in the cultures, kept at a temperature of about 30°, in from 8 to 14 days; in many cases a pure culture was produced. The bacteria are lively moving little rods of about 2 μ length and 1.5 μ thickness, peritrically ciliated. They grow both in inorganic nutrient solution with paraffin hydrocarbons as the sole carbon- and energy-source, as also in the usual organic rearing-grounds as broth, broth-agar, &c. The microbes contain catalase and secrete the enzyme diastase, but not lipase, urease and proteolytic enzymes.

Similarly *B. aliphaticum liquefaciens* can be isolated if, in the place of *n*-hexane, naphthenes such as cyclohexane and 1,3-dimethylcyclohexane is used. The two kinds of bacteria, which practically agree in their properties, are distinguished in so far, that *B. aliphaticum liquefaciens* secretes proteolytic enzymes — gelatine is liquefied — and lipase.

Paraffin bacteria, that are similarly obtained by means of paraffin oil, form on fluid substrata, vigorously moving little rods of from 4 to 6 μ long, and 2 μ thick, which often occur in long chains, often composed of 20 members. The bacteria excrete the diffusing enzyme lipase, also proleolytic enzymes, but not urease.

Tausz let these three kinds of bacteria act on pure synthetic hydrocarbons, and mixtures of paraffin with naphthene hydrocarbons in inorganic or organic nutrient solutions, and observed both with the naked eye, and microscopically, the growth phenomena shown by the bacteria. The following facts were noted: — *B. aliphaticum* and *B. aliphaticum liquefaciens* attack all paraffin hydrocarbons; of the olefines *n*-caprylene and hexadecylene[2]), but not hexylene; also neither naphthene nor benzene hydrocarbons. The paraffin bacterium attacks: — *n*-hexane and *n*-octane, not on the contrary the higher members hexadecane, triacontane and tetratriacontane; of the olefines not hexylene and caprylene, but hexadecylene; neither naphthene nor benzene hydrocarbons.

Quantitative experiments showed that the attacked hydrocarbons were completely destroyed by the bacteria, also in the presence of naphthenes, which remained unchanged.

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[1]) *Zentralbl. f. Bakteriol. u. Parasitenk. Abt. II.* 49 (1919), 497. As per kindly forwarded reprint. — [2]) Hexadecylene, $C_{16}H_{32}$, which was obtained by distilling spermaceti under reduced pressure, according to a prescription given by Tausz, was purified by converting into the mercury salt.

Hence we have in *B. aliphaticum* or *B. aliphaticum liquefaciens* a valuable reagent for testing the purity of naphthene hydrocarbons. Further, since even traces of admixed hydrocarbons were quantitatively removed from naphthene, the bacteria render it possible to prepare the last-named in a pure state. Tausz found on this occasion that the naphthenes prepared according to Sabatier were not pure, on account of the presence of aliphatic hydrocarbons.

The Tausz method up to the present has been applied to fractions of pressure distillates of artificial and natural lubricating oils, from which pure naphthene hydrocarbons could be isolated. Also in a fraction of a polymerisation product of amylene the absence of naphthenes could be proved, and in a fraction of Rumanian petroleum the absence of paraffin hydrocarbons.

Proof of the absence of terpene hydrocarbons in crude petroleum oils. — In addition to the naturally occurring terpenes, also those unsaturated hydrocarbons obtainable from terpene derivatives, or synthetically, are assigned to the group of the terpene hydrocarbons. All these hydrocarbons are distinguished by great chemical activity; mercury salts such as mercuric chloride or mercuric acetate dissolved in methyl alcohol or water react at ordinary temperatures with all terpenic compounds, but not with other hydrocarbons. The earlier experiments instituted by Balbiano[1]) on the behaviour of terpene hydrocarbons with mercury acetate have again been taken up by J. Tausz and H. Wolf[2]), but they could only partly confirm his results.

By reason of his investigations Tausz divides the hydrocarbons into 4 groups. To Group 1 belong those hydrocarbons which with alcoholic solutions of mercury acetate give mercury salts at ordinary temperature. These hydrocarbons which form their mercury compounds by substitution and addition of mercury salt and alcohol contain an active hydrogen atom joined to a doubly bound carbon atom. The hydrocarbons of Group 2 were only oxidised by an aqueous solution of mercury acetate at ordinary temperature. Group 3 comprises the aromatic hydrocarbons, which still contain a free hydrogen atom in the nucleus, and which form their mercury salts by substitution only, without an additive reaction, at a temperature of over 100°. To Group 4 belong the unsaturated compounds which neither form mercury salts, nor are oxidised by mercury compounds.

The fact that all the terpene hydrocarbons investigated by him, react with mercuric acetate solution, and hence belong either to group 1 or group 2, has been applied by Tausz to test raw petroleums for the presence of terpenes. Up to now it has only been proved that ethylene occurs in the mineral oil gas of Pechelbronn, hence that the first member of the olefine series is present in petroleum. There is numerous but mutually contradictory information in the literature on the occurrence of terpene-like hydrocarbons in mineral oils. Tausz has elaborated the following process to prove the presence of terpenes in petroleum oils: —

7 g. mercury acetate are dissolved in 75 cc. methyl alcohol, and added to the vacuum distillate (1 litre) of the mineral oil contained in a separating funnel of 3 litres capacity, and the whole shaken up for 10 minutes. Two layers are present in the vacuum distillate; the lower is methyl alcohol and water, and must contain the terpene-mercury compound, if present. The water-methyl-alcohol layer is run out; the upper layer is washed with methyl alcohol; the methyl alcohol is again run out and added to the former. The combined liquids are distilled *in vacuo*. The residue is tested for the terpene mercury compound.

[1]) Cf. *Report* April 1906, 100. — [2]) *Zeitschr. f. angew. Chem.* 32 (1919), I. 233.

By this method Tausz examined about a litre of each distillate, obtained in the Gäde-vacuum at 100°, of the following crude oils: — Raw oils of Bitkow, Kolomea, Rumania, Balachana, Alaska and Gogor (Java). No quicksilver salt of unsaturated hydrocarbons could be isolated. Hence there are no terpenes of group 1 present, hence neither the aliphatic hemiterpene *iso*prene, the aliphatic terpene myrcene, the aliphatic terpene-like compound methyl *iso*prene, nor the true terpenes pinene, dipentene, limonene, sabinene, camphene, also neither the sesquiterpene cubebene, nor the cyclic terpene-like compounds dihydrobenzene, tetrahydrobenzene, and methyltetrahydrobenzene. For purposes of control, 1 litre of the examined Gäde-vacuum distillate was treated with 0.5 to 1 cc. pinene or dipentene. This corresponds to a terpene content of 0.05 to 0.1 per cent. From this added terpene 0.6 or 1.3 g. mercury compound could be obtained, according to amount of terpene added, so that the limit of applicability of this method lies near 0.008 per cent.

Tausz than caused the same crude mineral oils to remain in contact with aqueous mercury acetate solution, with constant shaking for 2 weeks, in order to test for terpenes of group 2. The reaction was similarly unimportant; only insignificant quantities of mercuric acetate appeared.

In view of these facts Tausz came to the conclusion that, contrary to all the literary information, simple terpenes and terpene-like hydrocarbons do not occur in crude petroleums.

This finding agrees completely with our knowledge of the unsaturated hydrocarbons. Also if terpene-like compounds were once present in crude petroleum, then they could not remain as such, on account of their great reactivity and the ease with which they polymerise.

The chemistry of the higher hydrocarbons, which do not belong to the benzene series, has been little explored, in comparison with other domains of organic chemistry. As B. J. Brooks[1]) remarks in a treatise, that the difficulties of obtaining the higher aliphatic hydrocarbons in a state of purity are very great. A good bibliography also is wanting. Work has been done in this respect in Russia, but it has only become partially known.

Although petroleum probably contains all normal paraffin hydrocarbons up to $C_{26}H_{54}$, and perhaps beyond, it has been impossible up to now to obtain pure compounds from this raw material; syntheses also of such higher hydrocarbons have not yet succeeded. Young had to fractional-distil a mixture of pentane and *iso*pentane no less than 13 times, in order to obtain both the substances in a comparative state of purity. When, according to older works, a great number of hydrocarbons were alleged to have been isolated from petroleum and obtained pure, then the allegations were all wrong.

In many text books on organic chemistry a series of typical reactions for methane and its homologues is given. These reactions are mostly valid for the lower members of the series; but not for the higher. The Grignard reaction is not applicable for alkylhalides with more than six carbon atoms. Bromohexane give practically only dodecane, and hence reacts as follows: — $C_6H_{13}MgBr + C_6H_{13}Br = C_{12}H_{26} + MgBr_2$. Many known reactions fail with the higher paraffins on account of the instability of the alkylhalides. For which reason, the condensation of higher alkylhalides to hydrocarbons by means of metallic sodium occurs more easily than with the lower: —

[1]) *Chem. and metallurg. Engineering* 22 (1920), 933.

$2C_{10}H_{21}Hlg + 2Na = C_{20}H_{42} + 2NaHlg$. It is to be expected that in this reaction chlorides give a better yield than bromides or iodides.

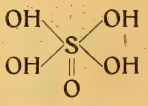
The higher alkylhalides have also the property — not yet more closely examined — of yielding saturated hydrocarbons (sometimes accompanied by ring-formation) when treated with alkali cyanides, alkali, aniline, &c., analogous to the formation of the cyclopropane ring by elimination of HBr from bromodimethylglutaric acid ester according to Perkin and Thorpe[1]: —

$$\begin{array}{l} CH_2\cdot CH_2\cdot CHH{-}R \\ \quad\vdots \\ CH_2\cdot CH_2\cdot CH_2Br \end{array} \longrightarrow \begin{array}{l} CH_2{-}CH_2{-}CH{-}R \\ \quad\vdots\quad\quad\vdots \\ CH_2{-}CH_2{-}CH_2 \end{array} + HBr$$

The properties of the ethylene linkages still hide a lot of unsolved problems. The addition of halogens, especially bromine, to the olefines, is a universal, characteristic reaction; and yet there exists a great difference in respect to the rapidity, and power of reaction between the substituted ethylenes. Whilst ethylene and propylene even at $-80°$ add bromine with a speed not to be measured, there are ethylene derivatives with strong electronegative groups (COOH, COOR, C_6H_5) which scarcely react with bromine, or not at all[2]).

Up to now it was assumed that the addition of water to olefines in dilute sulphuric acid, resulted exclusively from the hydrolysis of the alkylsulphuric acid ester in the following sense: —

$$\begin{array}{l} R\cdot CH_2 \\ \quad\vdots \\ R_1\cdot CH\cdot OSO_3H \end{array} + H_2O \longrightarrow \begin{array}{l} R\cdot CH_2 \\ \quad\vdots \\ R_1\cdot CH\cdot OH \end{array} + H_2SO_4$$



(I) Orthosulphuric acid.

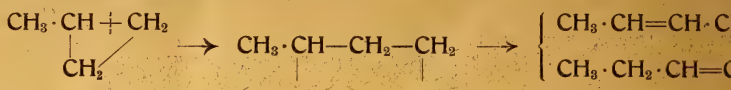
According to another, more modern view the hydration is explained by the temporary formation of the orthosulphuric acid ester (I). Also water alone reacts, in a very few cases, with compounds having doubled linkages, as with the ketenes $(R_2)C{=}CO$. Bodies containing the group $-CH{=}CH{-}C{=}O-$, as mesityl oxide, citral, pulegone, are often hydrolysed by diluted acids with the rupture of the chain. Further, compounds containing this group — as citral, citronellal — add on sodium bisulphite; the additive power for malonic acid ester, acetoacetic ester, hydrocyanic acid and unsaturated compounds of this kind is less well studied. It may be mentioned here, that the group $-CH{=}CH\cdot CO-$ determines the characteristic odour of many substances, such as that of violets.

A very general and yet little explained property of the olefines is their tendency to polymerise. When the process takes place in the presence of concentrated sulphuric acid, it can be explained by the formation of an alkylsulphuric acid ester: — on the other hand, the process of polymerisation under the influence of metallic sodium, heat and air is not explained. Here, without doubt, the fundamental properties of the molecule, and the theory of valency must be brought into consideration. Also the influence of heat and light on the vibrations of the electrons would have to be taken into account, and perhaps in connection therewith, the frequent changes of position of the double bonds.

Instability of structure is a striking characteristic of higher aliphatic compounds. *Iso*butyl alcohol and the primary *iso*butylhalides $(CH_3)_2CH\cdot CH_2X$ yield a mixture of *iso*butylene $(CH_3)_2C{=}CH_2$ and of β- and α-normal butylene $CH_3CH{=}CH\cdot CH_3$ and

[1]) *Journ. Chem. Soc.* **75** (1899), 48. — [2]) *Berl. Berichte* **37** (1904), 3317.

$CH_3 \cdot CH_2 \cdot CH{=}CH_2$. Nef assumed, for purposes of explanation, the temporary formation of a cyclopropane ring, which is easily split.



The striking rearrangements amongst the cyclic compounds — the 6-ring passing into a 7-ring; the 7-ring into an 8-ring, and *vice versa* have been thoroughly studied by Meerwein[1]) in his work on borneol and camphene.

The chemical investigation of the aliphatic hydrocarbons is of great value to industry. Searching experiments have shown that ethyl alcohol, acetaldehyde, acetone, glycol, chlorohydrin can be obtained in large quantities from oil gases. Attempts have also been made to utilise the unsaturated hydrocarbons of petroleum. The hydrogenation of these substances is technically very difficult, since the sulphur generally present in them renders the catalyst impure and useless. The olefines however, are easy to oxidise, and it is possible that in this manner they may be advantageously employed in the preparation of fatty acids[2]). An American petroleum company has recently taken up the preparation of a series of primary, secondary and tertiary alcohols from petroleum and oil gas olefines.

Not much, as yet, can be said with certainly on the origin of petroleum. Though Engler pointed out that in the destructive distillation of fats and fatty oils under pressure, a mixture mostly of hydrocarbons was obtained, which resembled petroleum, yet this does not furnish a proof of the formation of petroleum. Mineral oils are often found in completely unchanged strata, which has never come into contact with volcanoes and other heat sources, as in the lime rocks of Trenton (Ohio). It is certainly possible, that the reactions experimentally shown by Engler, also ake place at a lower temperature, and occupy long periods of time; but how saturated hydrocarbons were formed in nature in a bio-chemical way, is still unknown to us. For example, we know nothing certain about the formation of *n*-heptane in the turpentine of *Pinus Sabiniana*, Douglas, and of the paraffins in many volatile oils, as in rose oil. Perhaps it is a case of anærobic fermentation, as has been proved to occur in organic remains under water and mud — decomposition of cellulose to methane. Many micro-organisms, *e. g.*, tubercle bacilli form wax-like substances, and paraffin is regarded by Reichenbach as a decomposition product of wood.

Petroleum is further changed by the action of sulphur, air, and oxygen. Sulphur in tri-atomic form combines, according to Erdmann, directly with olefines to form the so-called thiozonides; and sulphur strongly heated with heavy hydrocarbons yields tar, or coke together with hydrogen sulphide. Although the structure of the valuable substance ichthyol is unknown, success has been achieved in preparing a product similar to Austrian ichthyol.

H. Stoltzenberg[3]) gives a process for obtaining terpenes and other products of the dry distillation of the defecation slime of the sugar factories. As soon after its formation as possible, and before decomposition has set in, the slime is dried without the addition of any substance, and then subjected to dry distillation. From the fraction of the defecation slime rich in rosin, large quantities of terpenes and rosin are obtained[4]); from the fraction rich in nitrogen many bases are obtained; and much acetone is obtained

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[1]) Cf. *Report* April **1915**, 90; **1919**, 133. — [2]) Cf. also the work of C. Harries, *Berl. Berichte* **52** (1919), 65. — [3]) D. R. P. 316503, Kl. 12[o]. As per *Chem. Zentralbl.* **1920**, II. 188. — [4]) Further information wanting.

from the fraction rich in fatty acids. The acetone, which is obtained along with acids, formed by the decomposition of the aqueous portion of the slime distillation, is almost pure, and contains no furfural.

For the purpose of amplifying earlier contributions[1]), K. v. Auwers[2]) published the results of fresh researches, especially on *cyclo*hexanes. By a series of examples he was able to confirm the validity of the rules laid down by him on the relations between constitution and physical properties of hydroaromatic compounds, and to dispose of a few apparent exceptions to these rules. According to earlier data, the 1,1,3-trimethyl*cyclo*hexane was said to possess the lowest density of the 3 trimethyl-*cyclo*hexanes investigated, although as a rule, the specific gravity usually rises with increase of methyl groups. The latest re-examination has shown that, as a matter of fact, this exception does not exist. In studying the 1,2,4,5-tetramethyl*cyclo*hexane it turned out that a preparation which was obtained from hexahydro*pseudo*cumene according to the method of Sabatier, agreed in its constants with the rule. On the contrary, a tetramethyl*cyclo*hexane prepared by reduction of durene with platinum and hydrogen, in the presence of glacial acetic acid, according to the method of Skita and Willstätter — on account of its properties, fell far away from the series of all other *cyclo*hexanes. By searching experiments on structurally related simpler material (*pseudo*-cumenol), the proof was able to be produced, that the two different hydrogenating methods led to widely different forms of the *cyclo*hexane derivatives. The products of hydrogenation after the method of Skita and Willstätter, if methylated many times, possess higher densities and refractive indices than those obtained by Sabatier's method; but on the contrary, lower molecular refractions. From the formerly established rules it is to be inferred that the substituents lie closer to one another in the former products; that is they consist mostly of *cis*-modifications, whilst the more violent Sabatier process yields more *trans*-modifications.

The constants of the preparations investigated and the methods of obtaining them — *cyclo*hexanes, *cyclo*hexenes, *cyclo*hexanols, *cyclo*hexanones — are to be found in the experimental section of the work.

Cymene. — By the direct nitration of cymene, O. Aschan and Teräsvuori[3]) obtained a small yield of 2-mononitrocymene ($d_{25°}$ 1.067). Further Aschan and Per Ekkwall allowed cymene, with constant stirring, to drop into strongly cooled nitric acid (d 1.52), and obtained, by means of repeated fractional crystallisation: — (1). The compound $C_{18}H_{17}O_{10}N_5$ (m. p. 70°), yellow needles soluble in benzene, which yielded an amine on reduction with ammonium sulphide. (2). 3,5-dinitro-*p*-cymene (m. p. 54°), white-green tablets, soluble in hot alcohol, which were converted into nitrocarvacrylamine on reduction. In diazotising this amine nitrocarvacrol (m. p. 116 to 117) appeared as by-product. (3). The nitro compound $C_{10}H_{12}O_5N_2$ (m. p. 90 to 91°), prisms or tablets; which probably represented the dinitrohydroxy compound of *p*-cymene, perhaps having the formula $C_6H_2CH_3[1](NO_2)_2[2,6]\cdot C(OH)(CH_3)_2[4]$.

$\Delta^{1,6}$-m-Menthadiene. — G. G. Henderson and T. F. Smeaton[4]) obtained a *m*-menthadiene containing two ethylene linkages in the benzene ring. From *m-iso*cymene via the sulphonic acid, they first prepared 6-hydroxy-*m-iso*cymene (b. p. 231°), which was further worked up into *$\Delta^{1,6}$-m*-menthadiene, according to the process described by Henderson and Schotz

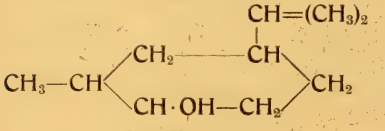
[1]) Cf. *Report* October 1915, 62. — [2]) *Liebig's Annalen* **420** (1920), 84. — [3]) *Finska Kemistsamfundets Meddelanden.* As per *Chem. Zentralbl.* **1919**, I. 227. — [4]) *Journ. chem. Soc.* **117** (1920), 144.

for the synthesis of menthadienes from thymol and carvacrol[1]). The method may be shortly reproduced here: — Reduction with finely divided nickel to *m*-menthan-6-ol (b. p. 119 to 121° [28 mm.]; $d_{20°}$ 0.9156; $n_{D20°}$ 1.4666; mol.-refr. 47.30); splitting off of water by heating with oxalic acid gives Δ^5-*m*-menthene (b. p. 167 to 168°; $d_{20°}$ 0.8222; $n_{D20°}$ 1.4568; mol.-refr. 45.61); preparation of *m*-menthene dibromide; conversion into $\Delta^{4,6}$-*m*-menthadiene by means of alcoholic potash.

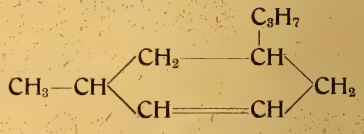
The hydrocarbon $C_{10}H_{18}$ obtained from *m*-menthan-6-ol (I) might be either Δ^5-*m*-menthene (II), or Δ^6-menthene (III). The constitution of this compound could not be found directly. But it agrees in its properties with a substance obtained by Knoevenagel from *m*-menthan-5-ol, which was either Δ^4-*m*-menthene, or Δ^5-*m*-menthene. It follows all the more probably from this that a Δ^5-*m*-menthene was present. The final product obtained must be according to this, a $\Delta^{4,6}$-*m*-menthadiene (IV).

The compound is a colourless, pleasant smelling liquid (b. p. 169 to 171°; $d_{20°}$ 0.8515; $n_{D20°}$ 1.47270; mol. refr. 44.89; calculated 45.24). With sulphuric acid it gives a red; with sulphuric acid and alcohol, a reddish-brown; and with acetic anhydride and sulphuric acid a violet coloration. The substance probably polymerises on keeping. After 7 days the purified compound had the following constants: — $d_{20°}$ 0.8614, $n_{D20°}$ 1.47437, mol. refr. 44.44.

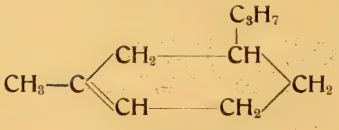
The fact that the hydrocarbon only adds on one molecule of bromine, points to the presence of two conjugated double linkings. The molecular refraction was indeed normal and the exaltation to be expected was not forthcoming; the molecular dispersion on the contrary, speaks for the conjugated system. The observation stands in agreement with the statements of von Auwers and Eisenlohr[2]), according to which the presence of conjugated double linkages is to be inferred much rather from the molecular dispersion than from the molecular refraction.



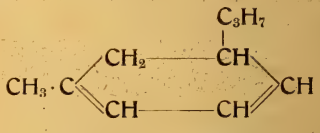
(I) *m*-Menthan-6-ol.



(II) Δ^5-*m*-Menthene.



(III) Δ^6-*m*-Menthene.



(IV) $\Delta^{4,6}$-*m*-Menthadiene.

Pinene. — Catalysts, such as finely divided metals, lower the temperature necessary for a reaction and hasten double-decomposition reactions. Starting from these facts, P. Sabatier, A. Mailhe, and G. Gaudion investigated the action of finely divided copper, nickel, cobalt, and iron on pinene vapours[3]).

The pinene was obtained from French turpentine oil by choosing the fraction passing over at 156 to 158°, and had the following properties: — $d_{15°}$ 0.87; $[\alpha]_D$ — 36° 8′. When the pinene vapours were led over the metals, reduced from their oxides, at 350°, a liquid was obtained, without the generation of gases, of boiling point 156 to 230°, which consisted almost wholly of pinene isomerides, together with small quantities of

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[1]) Cf. *Report* April **1913**, 136. — [2]) *Berl. Berichte* **43** (1910), 80. — [3]) *Compt. rend.* **168** (1919), 926.

polyterpenes. At higher temperatures smaller or larger quantities of gas were developed, according to the kind of catalyst used.

The pinene vapours led over copper at 500°, yielded a gas burning with a luminous flame, and rich in hydrogen and ethylene hydrocarbons, together with a greenish liquid. In the distillate obtained at 600 to 630° were found benzene in small quantities, also toluene, *m*-xylene (b. p. 139°, d 0.871), *iso*prene (?) or piperylene (?), hexenes, terpenes, ethylene- and diethylene hydrocarbons, and above all, in the chief fraction, cymene (b. p. 175°), together with cumene, methylethylbenzene, and terpenes isomeric with pinene (b. p. 170 and over 180°). Altogether about 31 per cent. of aromatic hydrocarbons, capable of being isolated as nitro compounds, were obtained from the pinene.

Since nickel had a hydrogenating effect, the reaction product obtained at about 600° contained more saturated hydrocarbons; in the fraction 150 to 180°, a terpane was found together with cymene. Whilst cobalt in its action at 600° resembled partly the copper and partly the nickel, the same results were obtained with iron as with nickel.

Terebene. — The reaction product of concentrated sulphuric acid on turpentine oil — the so-called terebene — has belonged since 1890 to the preparations of the American pharmacopœia, and since 1890 to those of the British pharmacopœia. In the current editions of both books the fixed constants of terebene are given — the boiling point, specific gravity and the specific rotatory power[1]). In very few cases, according to B. F. Howard[2]), does the terebene prepared according to rule agree with these constants, since the raw material is seldom the same.

Howard reports that during the years 1913 to 1919 the American turpentine oil used for the preparation of terebene had continually varying constants. The specific rotatory power especially varied between +18 and −30°. Hence it is explainable, that the terebenes in most cases were also obtained with various specific rotatory powers.

By reason of his investigations and observations Howard concludes that the decisive test for the purity of terebene is the boiling point alone — not the specific rotatory power and the specific gravity. The data of the pharmacopœia ought therefore to be modified as follows.

"Description: — Terebene is a mixture of dipentene and other hydrocarbons, obtained by shaking up turpentine oil with sufficient quantities of sulphuric acid gradually added, till the reaction product, after steam distillation, has the boiling point given below.

Criterion and testing: — A colourless liquid, pleasant odour, aromatic taste similar to that of turpentine, specific gravity 0.854 to 0.862; soluble in 5 parts 90 per cent. alcohol; the boiling point, particularly, 165 to 185° (below 160° only 5 per cent. of the preparation, at the most, should boil) leaving behind a small amount of a thick fluid residue; absence of rosin. Data on optical rotatory powers ought not to be required."

Camphene. — G. Langlois[3]) has published exhaustive researches on the isomerism in the camphene series. In order to name the numerous camphene derivatives he designates the radicles derivable from camphenilane C_9H_{16} (I), *viz.*, C_9H_{15} (II) and C_9H_{14} (III) as camphenilene[4]). and camphenilidene, respectively. According to this, camphene (IV) might even be called camphenilidene-6-methane. For the products of

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[1]) Cf. *Report* October **1905**, 78; October **1915**, 49; **1918**, 58. — [2]) *Pharmaceutical Journal* **103** (1919), 76. — [3]) *Annal. de Chim.* **12** (1919), 193 to 363. According to kindly forwarded reprint. — [4]) According to customary nomenclature, the name "camphenilene" is given to the hydrocarbon C_9H_{14}, which was obtained by Moycho and Zienkowski. *Liebig's Annalen* **340** (1905), 53.

intramolecular change the numeration of Bredt is retained. The general results to which the work led are as follows:—

All substitutions in camphor took place in the methylene group 6, where the one hydrogen atom is easily replaceable. This fact, already discovered by Lipp[1]) in nitrocamphor, was generally confirmed by Langlois in the bromine and chlorine derivatives, and in a new compound — methylol camphene. The camphene molecule, otherwise prone to intramolecular change, became less capable of reaction by these substitutions. Thus chloro-, bromo- and methyl camphene were unchanged on mixing with chromic acid, and also with hydrochloric acid in the cold.

On oxidising with potassium permanganate, the substitution products yielded, in almost all cases, camphenilone (V), with rupture of the double bond, by which also the camphene nature of the compound was demonstrated. On the contrary, the compounds with two camphene rings, as dicamphenilidene butane $C_9H_{14}:CH\cdot CH_2CH_2CH:C_9H_{14}$ and bicamphenilidene diethyl ether $C_9H_{14}:CH\cdot CH_2\cdot O\cdot CH_2CH:C_9H_{14}$, are stable in the presence of potassium permanganate, even on the water bath. Hence for the last-named an oxonium structure can be assumed $\dot{C}H\cdot CH\cdot CH:O:CH\cdot CH\cdot\dot{C}H$. Yet even here also through gradual disintegration, first with chromic acid mixture, camphenilidene acetaldehyde and camphene carboxylic acid can be obtained; and finally camphenilone by means of permanganate.

In studying the halogen derivatives it became apparent that a camphene dichloride[2]) did not exist. Addition compounds could be obtained by the action of bromine and chlorine on bromo- and chlorocamphene. Hydrogen bromide was added on, accompanied by rearrangement which led to derivatives of the camphor type.

The winning of dehydro dicamphene $C_9H_{14}:CH\cdot CH:C_9H_{14}$ from bromocamphene, and pentenyl camphene $C_9H_{14}:CH\cdot CH:C_4H_8$ — a sesquicamphene — from camphenilidene acetaldehyde should also be noted. By condensation of camphenilidene acetaldehyde with acetone the ketone $C_9H_{14}:CH\cdot CH:CH\cdot CO\cdot CH_3$ was obtained, which was very stable in the presence of chromic acid solution. This behaviour agrees with Thiele's theory of the conjugated double bonds, and the mutually neutralising partial valencies

$$\dot{C}=CH-CH=CH-C(CH_3)=O.$$

Amongst the compounds described by Langlois are many isomerides with the constituents of sandalwood oil, and the disintegration products of santalol.

Langlois used, as starting material, a camphene with the constants: — m. p. 42°; b. p. 158 to 160°; $\alpha_D + 58.2°$. ω-bromocamphene $C_9H_{14}CHBr$ (b. p. 225 to 226°; b. p. 115 to 120° [15 mm.]; $d_{15°}$ 1.265; $\alpha_D + 68.85°$) was obtained by heating camphene dibromide with dimethylaniline to 180°. On passing chlorine into the ether solution of bromocamphene, bromocamphene dichloride (VI) [m. p. 74°] was produced; and on passing hydrobromic acid into bromocamphene he obtained the unstable camphene dibromide $C_{10}H_{16}Br_2$ (VII) [m. p. 90°], which, under the assumption of an internal rearrangement in opposition to Semmler[3]), he formulated as 2-bromo-ω-bromocamphane. On heating, it is decomposed into bromocamphene and hydrobromic acid. The same camphene dibromide was obtained by passing bromine-free hydrochloric acid into a hot glacial acetic acid solution of bromocamphene. Langlois assumes

[1]) Cf. *Report* April 1914, 129. — [2]) Semmler reports that by the action of chlorine on camphene the compound $C_{10}H_{15}Cl\cdot HCl$ is produced in addition to chlorocamphene $C_{10}H_{15}Cl$. *Berl. Berichte* **35** (1902), 1021. — [3]) Cf. *Berl. Berichte* **33** (1900), 3426.

that the hydrochloric acid catalytically sets free hydrobromic acid from part of the bromocamphene with the resinification of the $C_{10}H_{14}$-radicle. The last-named combines with the still unchanged bromocamphene.

By treatment of bromocamphene with magnesium in the presence of CO_2 and a little ethyl bromide, dehydro dicamphene $C_9H_{14}:CH\cdot CH:C_9H_{14}$ (m. p. 181°) and camphene carboxylic acid $C_9H_{14}:CH\cdot COOH$ (m. p. 124 to 125°) were obtained. The last-named yielded camphenilone on oxidation (m. p. 223 to 224°).

In a similar manner to bromocamphene Langlois prepared the ω-chlorocamphene (b. p. 95 to 98° [15 mm.]; $d_{15°}$ 1.016 to 1.017; $\alpha_D + 37°$), which with hydrobromic acid gas yielded 2-bromo-ω-chlorocamphane (VIII) $C_{10}H_{16}BrCl$ (m. p. 103°), but which did not add on any hydrochloric acid gas. The camphene dichloride of literature is hence according to Langlois to be crossed out. Trichlorocamphene $C_{10}H_{15}Cl_3$ (m. p. 104°) and chlorodibromocamphene $C_{10}H_{15}Cl\cdot Br_2$ (m. p. 64 to 65°) were also prepared. From camphene, trioxymethylene, and glacial acetic acid Langlois obtained the acetate of ω-methylol camphene. The alcohol itself ($C_9H_{14}:CH\cdot CH_2OH$) had the constants:— b. p. 234 to 238°, $d_{15°}$ 0.987 to 0.988, $\alpha_D + 45°$; it added on two atoms of bromine in neutral solution and formed the above-mentioned camphene dibromide. The semicarbazone of the ω-methylolcamphene pyroracemic acid ester melted at 167°. On continually heating ω-methylol camphene with alcoholic potash *bis*-β,β'-camphenilidene-6-diethyl ether $C_9H_{14}:CH\cdot CH_2\cdot O\cdot CH_2CH:C_9H_{14}$ (b. p. 235 to 240° [25 mm.], $d_{20°}$ 0.983) was produced. Whilst on shaking the alcohol with alkaline (Na_2CO_3) and permanganate, camphenilone, hydroxycamphenilanic acid $C_9H_{14}\cdot OH\cdot COOH$ (m. p. 184°) and oxalic acid were produced; an intramolecular rearrangement partly resulted on treating with potassium permanganate rendered alkaline with caustic alkali. Camphenecamphoric acid was chief product accompanied by camphenilone and oxalic acid.

ω-Chloromethyl camphene $C_9H_{14}:CH\cdot CH_2Cl$ (b. p. 100 to 102° at 6 mm.; $d_{15°}$ 1.020; $[\alpha]_D + 27.38°$) was obtained together with the corresponding oxide from methylol camphene; it yielded camphenilone with potassium permanganate; and with chromic acid mixture and by autoxidation, camphene carboxylic acid $C_9H_{14}:CH\cdot COOH$ and a little camphenilidene-6-acetaldehyde $C_9H_{14}:CH\cdot CHO$. Under the same conditions, under which here only the side-chains were attacked, methyl camphene underwent no change, whilst on the contrary, camphene suffered a radical alteration. On attempting to reduce with sodium and alcohol, ω-chloromethyl camphene exchanged its chlorine atom for the OC_2H_5 group and formed camphenilidene-6-ethoxyethane $C_9H_{14}:CH_2O\cdot C_2H_5$ (b. p. 230°; $\alpha_{D15°}$ 0.917). After keeping for 4 years the substance had changed into camphene carboxylic acid and camphenilidene-6-acetaldehyde by autoxidation.

On the other hand chloromethylcamphene, when treated with zinc and hydrochloric acid, was able to exchange its chlorine atom for hydrogen. The 6-methylcamphene had the constants:— $d_{15°}$ 0.880, $[\alpha]_D + 4.28°$. Further, the chlorine atom was exchanged for CN with the formation of a nitrile $C_9H_{14}:CH\cdot CH_2CN$ (b. p. 140° [12 mm.]). On saponification, the nitrile, in consequence of partial migration of the double bond, yielded a mixture of two isomeric acids to which the formulæ $C_9H_{14}:CH\cdot CH_2\cdot COOH$, and $C_9H_{15}\cdot CH:CH\cdot COOH$ may probably be assigned. By the action of sodium or magnesium on an ether-solution of ω-chlormethylcamphene (Wurtz Reaction), the dicamphenilidene butane $C_9H_{14}:CH\cdot CH_2\cdot CH_2\cdot CH:C_9H_{14}$, was obtained after 4 to 5 days as a thick oil (b. p. 210°, $d_{15°}$ 0.952, $[\alpha]_D + 67.3°$), which in chloroform added bromine. From ω-chloromethylcamphene and sodium camphene methylate $C_9H_{14}:CH\cdot CH_2ONa$ the symmetrical ether $C_{11}H_{17}\cdot O\cdot C_{11}H_{17}$ (b. p. 235° at 25 mm.; $d_{15°}$ 0.93) was obtained. Oxidation of camphenilidene-6-ethanol with chromic acid mixture yielded, in addition

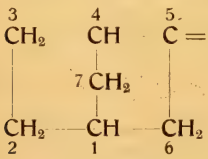
to camphenecarboxylic acid, the camphenilidene-6-ethanal $C_9H_{14}:CH\cdot CHO$ (b. p. 130° at 12 mm.; $d_{15°}$ 1.002; $[\alpha]_D$ +72.58°; m. p. of the semicarbazone 233°). Although a CH-group is present near to the aldehyde group, no enolisation resulted. On the contrary, a diacetate could be obtained with sulphuric acid as a catalyst. By way of the oxime and the nitrile of the aldehyde (both oily), the corresponding acid amide, m. p. 192° was obtained. The saponification did not result in the acid.

Camphenecarboxylic acid was transformed by continued heating on the water bath into pure semicyclic *d,l*-camphene (b. p. 158 to 160°; m. p. 45 to 46°). On treatment of the acid — which was characterised by several derivatives, as the ethylester, chloride and amide — with sodium and amylalcohol, Langlois obtained *d.l-iso*camphanecarboxylic acid $C_9H_{15}\cdot CH_2COOH$ (b. p. 165 to 168° at 20 mm., m. p. 75 to 76°, unsharp).

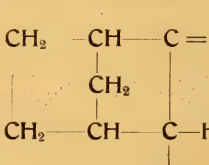
The reduction of camphenilidene-6-acetaldehyde with zinc and hydrochloric acid on warming (Clemmenssen's method) yielded *ω*-methylcamphene (b. p. 178°; $d_{15°}$ 0.884; $[\alpha]_D$ +4°), which is not identical with the homocamphene obtained by Wallach[1]) from methylborneol. The greater part of the homocamphene remained unchanged on treatment with chromic acid mixture and with hydrochloric acid gas; an intramolecular change resulted on treating with hydrobromic acid gas, and there resulted 2-bromo-*ω*-methylcamphane (IX) (b. p. 108 to 110° at 17 mm; $d_{15°}$ 1.175).

Condensation of the aldehyde with acetone and butanone by means of sodium alcoholate led to the ketones camphenebutenone $C_9H_{14}:CH\cdot CH:CH\cdot CO\cdot CH_3$ (b. p. 160° at 12 mm., $d_{15°}$ 0.980) and camphenepentenone $C_9H_{14}:CH\cdot CH:CH\cdot CO\cdot C_2H_5$ (b. p. 172 to 175° at 12 mm.; $d_{15°}$ 0.968), which are characterised by three conjugated double bonds; it was possible to obtain the semicarbazones (m. p. 220 to 221° and 209 to 210°), but no sodium bisulphite compound.

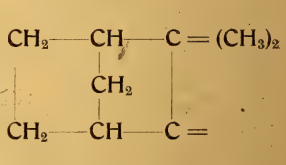
Finally, the aldehyde and the magnesium-halogen-alkyl compounds further yielded the hydrocarbons ethenyl camphene $C_9H_{14}:CH\cdot CH:CH_2$ (b. p. 203 to 205°; $d_{15°}$ 0.921; $[\alpha]_D$ +76.39°); propenyl camphene $C_9H_{14}:CH\cdot CH:CH\cdot CH_3$ (b. p. 230 to 232°; $d_{15°}$ 0.919; $[\alpha]_D$ +70°), butenyl camphene $C_9H_{14}:CH\cdot CH:C_3H_6$ (b. p. 238 to 240°; $d_{15°}$ 0.905; $[\alpha]_D$ +80°) and pentenyl camphene (sesquicamphene) $C_9H_{14}:CH\cdot CH:C_4H_8$ (b. p. 255°; $d_{15°}$ 0.900; $[\alpha]_D$ +73°). For these four hydrocarbons the different behaviour of the two double bonds was characteristic. On oxidising with chromic acid mixture the semicyclic double bond remained whilst the other was broken. Two aldehydes were produced as reaction products (*e. g.* $C_9H_{14}:CH\cdot CHO$ and HCHO).



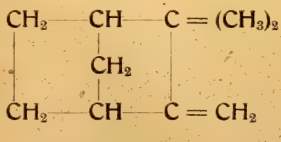
(I) Camphenilane.



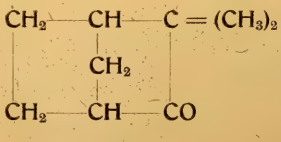
(II) Camphenilene (Radicle). Formula according to Langlois.



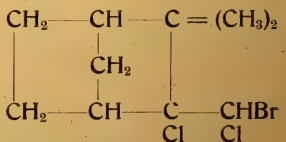
(III) Camphenilidene (Radicle) Formula according to Langlois.



(IV) Camphene.

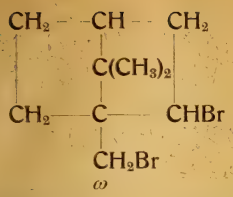


(V) Camphenilone.

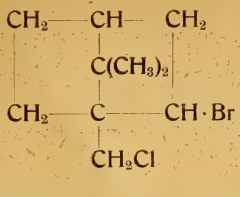


(VI) Bromocamphene dichloride.

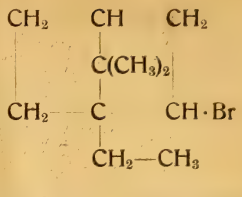
[1]) Cf. *Report* October 1907, 139.



(VII) 2-Bromo-ω-bromocamphane (camphene dibromide).



(VIII) 2-Bromo-ω-chlorocamphane.



(IX) 2-Bromo-ω-methylcamphane.

Carene. — The turpentine oil obtained in India from the turpentine of *Pinus longifolia*, Roxb., passes for a poorer product than the American oil. Nevertheless, it is much used, and the turpentine oil industry in Jallo (Punjab) and in Barely (United Provinces) is developing satisfactorily. According to earlier works[1]) the oil contains *l*-α-pinene, β-pinene, a sesquiterpene, and a terpene which on treatment with hydrochloric acid gives sylvestrene hydrochloride.

Since there was a supposition that sylvestrene is not originally present in the oil, but that it is the transformation product of an isomeric terpene, J. L. Simonsen[2]) examined once more the Indian turpentine oil for its ingredients. In the oil obtained from the factory at Jallo ($d^{30°}_{30°}$ 0.8717; α_D — 2.38°; $n_{D30°}$ 1.4725; acid value 2.4), he was able to confirm the presence of *l*-α-pinene, β-pinene and a tricyclic sesquiterpene. In addition, he found a new bicyclic terpene which he named "*d*-carene".

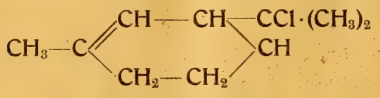
For investigation purposes Simonsen separated the oil into 3 fractions: — up to 118° at 200 mm. 31 per cent.; 118 to 130° at 200 mm. 47 per cent.; 149 to 155° at 36 mm. 19.2 per cent.; loss and residue 11.2 per cent. Two distillates were obtained from these fractions. (1) Between 155 and 167° (60.8 per cent.), containing the pinene. (2) Between 167 and 171° (14.8 per cent.), from which after repeated fractionation, *d*-carene (b. p. 123 to 124° at 200 mm.) was obtained. This terpene had the following properties: — b. p. 168 to 169° at 705 mm.; $d^{80°}_{30°}$ 0.8586; α_D + 7.69°; $n_{D30°}$ 1.469; mol.-refr. 44.23 (reckoned for $C_{10}H_{16}$ 43.5). *d*-Carene was a colourless oil with a characteristic, sweet smell. The solution in acetic anhydride gave a temporary green coloration on the addition of one drop of concentrated sulphuric acid. In contrast with sylvestrene and terpinene, carene was not attacked by chromic acid mixture. It was very easily oxidised by the air. No stable nitrosochloride or nitrosite could be obtained, but a crystalline nitrosate, however, which decomposed at 141.5°. Also no hydration resulted on long treatment with dilute sulphuric acid. Treated with dry hydrochloric acid, carene formed *d*-sylvestrene hydrochloride (I); treated with liquid hydrochloric acid it yielded a mixture of sylvestrene and dipentene hydrochlorides (II).

From these facts, one of the formulæ (III), (IV) or (V) could be assigned to carene. On oxidation of the terpene in ice-cold NaOH solution with potassium permanganate, a glycol was formed $C_{10}H_{18}O_2$ (m. p. 69 to 70°), (VI) or (VII). Since this glycol contained no primary-alcohol group, only the formulæ (III) and (IV) come into consideration; not however (V). Further, the generation of dimethyl malonic acid in the acid oxidation of the terpene, proved that the group $(CH_3)_2\begin{smallmatrix}C\cdot\\ |\\ C\cdot\end{smallmatrix}$ is present in the compound. In oxidising with potassium permanganate according to the method of von Baeyer and Ipatiev[3]) for

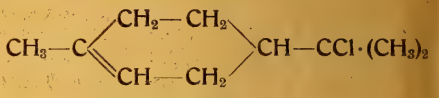
[1]) Cf. *Report* April 1911, 116; October 1911, 93. — [2]) *Journ. chem. Soc.* 117 (1920), 570. — [3]) *Berl. Berichte* 29 (1896), 2796.

obtaining caronic acid, *trans*-caronic acid was finally obtained. This evidence leaves no doubt that the constitution of carene corresponds to one of the two formulæ (III), (IV). The normal molecular refraction of the terpene points to the absence of a conjugated position of the double bond to the three-ring, and hence speaks for formula (III). Carene is the only terpene found in nature up to now with a carane-ring.

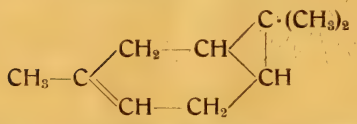
From the 149 to 155° (36 mm.) fraction of the original oil, the sesquiterpene named by Simonsen "*d*-longifolene" was obtained, after repeated distillation, as a colourless, rather viscid oil with a weak, not unpleasant smell, and the following constants:— b. p. 254 to 256° (706 mm.), 150 to 151° (36 mm.), $d^{30°}_{30°}$ 0.9284, $[\alpha]_D$ + 42.73°, $n_{D30°}$ 0.495, mol.-refr. 64.15. The molecular refraction leads to the conclusion of the tricyclic nature of the compound. With the halogen acids *d*-longifolene yielded beautiful crystalline derivatives; the melting point of the hydrochloride lay between 59 to 60°, that of the hydrobromide between 69 to 70°, and the hydriodide melted at about 71°.



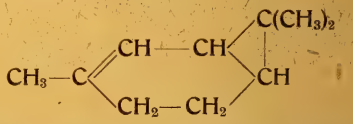
(I) Sylvestrene hydrochloride.



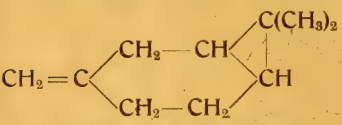
(II) Dipentene hydrochloride.



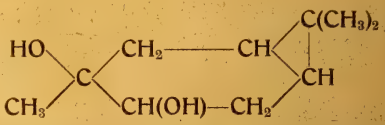
(III) 4,7,7-Trimethyl-bi*cyclo*-[0,1,4]-Δ^3-heptene. Probable formula of carene (Δ^3-carene).



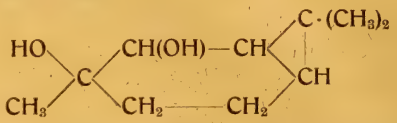
(IV) 4,7,7-Trimethyl-bi*cyclo*-[0,1,4]-Δ^4-heptene.



(V) 4-Methylene-7,7,-dimethyl-bi*cyclo*-[0,1,4]-$\Delta^{4(8)}$-heptene, dehydrocarane.



(VI) 4,7,7-Trimethyl-3,4-dihydroxy-bi*cyclo*-[0,1,4]-heptane.



(VII) 4,7,7-Trimethyl-4,5-dihydroxy-bi*cyclo*-[0,1,4]-heptane.

Tricyclene.—P. Lipp[1]) reports on attempts to obtain tricyclene (II) itself, by starting with tricyclenic acid. It was first intended to convert the ω-aminotricyclene (III), which is easily obtained from the nitrile of tricyclenic acid, into the corresponding alcohol by means of nitric acid. But instead of tricyclol, an oily complex product appeared which had been formed by the rearrangement of the ring system. This easily resulting rearrangement was understandable from the fact that the ω-aminotricyclene hydrochloride, warmed for a short time with fuming hydrochloric acid, easily yielded camphenilanaldehyde (IV), and ammonia.

A second series of attempts, starting with the methyl ester of tricyclenic acid, was more successful. The ester could be reduced to tricyclol (V) (m. p. 111—112°), giving

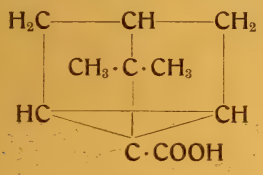
[1]) *Berl. Berichte* **53** (1920), 769.

a moderate yield; and was then converted, by means of chromic acid in glacial acetic solution, into the corresponding aldehyde, the tricyclal (VI) (m. p. 85—90°). This latter could be easily re-oxidised to tricyclenic acid; hence no rearrangement had taken place. This aldehyde, which is easily oxidised by atmospheric air, was condensed by Lipp without further purification, with hydrazine to the well crystallising aldazine (VII) (m. p. 171—172°); he placed this along with excess hydrazine in the pressure tube, and converted it to the monohydrazone (VIII), and finally obtained, as per Kishner and Wolff (heating with sodium ethylate to 180—195° under strong pressure), the tricyclene (m. p. 64—65°), almost quantitatively by the splitting-up of the hydrazone.

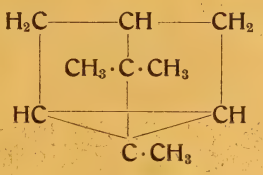
The hydrocarbon was only stable for a short time in cooled glacial acetic solution in the presence of permanganate; on gentle heating it yielded tricyclenic acid and a carbonyl compound as oxidation products. This showed that the splitting-up of the hydrazone had taken place normally, and that tricyclene, and tricyclenic acid have the same ring system.

Of interest also was the fact that tricyclene, under the same experimental conditions as borneol (digesting with sodium bisulphate at 160°), but not like *iso*borneol (digesting in benzene solution with zinc chloride), yielded the final product camphene. Hence tricyclene can be regarded as an intermediate product in the formation of camphor from borneol; not however as intermediate product in the splitting off of water from *iso*borneol. Thus the Wagner rearrangement, as Ruzicka[1]) seems to assume, cannot be schematised by introducing a tricyclene—the symmetrical tricyclene to wit—as an intermediate stage in the manner of formation of ordinary camphene.

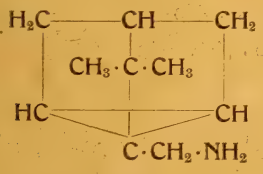
According to Meerwein[2]), the addition phenomena in the interchangeable transition of *iso*borneol to camphene is to be traced to the existence of a tautomerism between the esters of *iso*borneol and camphene hydrate.



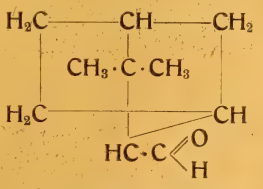
(I) Tricyclenic acid.



(II) Tricyclene.



(III) ω-Aminotricyclene.



(IV) Camphenilane aldehyde.

(V) Tricyclol. (VI) Tricyclal. (VII) Tricyclal aldazine.

(VIII) Tricyclalmonohydrazone. Tricyclene.

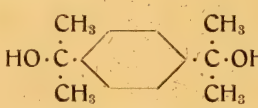
[1]) *Helvetica chimica acta* **1** (1918), 124, 130; *Report* **1919**, 115. — [2]) *Zeitschr. f. angew. Chem.* **33** (1920), II. 365.

*Synthesis of Derivatives of 1,4-Di-*isopropyl-cyclohexane. — M. T. Bogert and C. P. Harris[1]) met with new unsaturated hydrocarbons closely related to the terpenes, by treating the methyl ester of terephthalic acid and also its dihydro and tetrahydro derivatives with methyl-magnesium-iodide. In one case tetramethyl-*p*-phenylene glycol (I) was isolated as first reaction product, which on heating with potassium bisulphate was transformed into 1,4-di*iso*propenylbenzene (II); the glycols (III and V) originating from the di- and tetrahydro compounds of the terephthalic acid ester, immediately gave up water and formed 1,4-di-*iso*propenyl-$\Delta^{1,4}$-dihydrobenzene (IV) and two isomeric hydrocarbons of the formula $C_{12}H_{18}$ (VI, VII).

The di*iso*propenyl-benzene, as a simple diolefine, took up four atoms of bromine without any development of hydrobromic acid. Hence it should contain no conjugated double bond. But its enhanced molecular refraction pointing to 2 conjugated double bonds, and its magnetic rotatory power indicating 5 such systems, speak against this assumption. If the centric benzene formula be assumed as coming nearest to the truth, so should the Dewar formula, according to Bogert and Harris, be regarded as the phase which the centric formula in *iso*propylbenzene (VIII) would take.

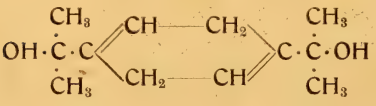
The 1,4-di*iso*propenyl-$\Delta^{1,4}$-dihydrobenzene $C_{12}H_{16}$ resembled the $\Delta^{1,4}$-terpadienes, reduced permanganate in the cold, added 4 atoms of bromine, and more still by substitution; the two forms — solid and liquid — of the tetrabromide represent *cis*- and *trans*-isomerides. Both the behaviour of the 1,4-di*iso*propenyl-$\Delta^{1,4}$-dihydrobenzene with bromine, and the increased molecular refraction, and magnetic rotatory power indicate that 2 conjugated double bonds were present.

No pure bromine derivative could be obtained from the two isomeric hydrocarbons $C_{12}H_{18}$, which were very sensitive to this element. It also could not be determined whether structural or stereo-isomerism was present. The behaviour of the compounds with bromine led also to the conclusion that conjugated double bonds were present. In molecular refraction and magnetic rotatory power, the hydrocarbon $C_{12}H_{18}$ resembled $\Delta^{1,8}$-dihydrobenzene, the dispersion of which had an exaltation of 20 per cent. (Harries and Willstätter[2]).

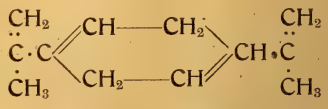


(I) 1,4-Di-[α-hydroxydimethomethyl]benzene.

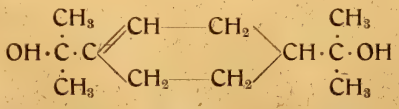
(II) 1,4-Di*iso*propenylbenzene.



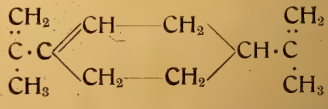
(III) 1,4-Di-[α-hydroxydimethomethyl]-$\Delta^{1,4}$-dihydrobenzene (cannot be isolated).



(IV) 1,4-Di*iso*propenyl-$\Delta^{1,4}$-dihydrobenzene.



(V) 1,4-Di-[α-hydroxydimethomethyl]-Δ^{1}-tetrahydrobenzene (cannot be isolated).



(VI) 1,4-Di*iso*propenyl-Δ^{1}-tetrahydrobenzene.

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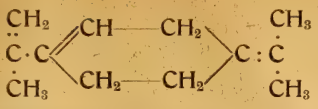
[1]) *Journ. Amerie. chem. Soc.* **41** (1919) 1676. — [2]) *Berl. Berichte* **45** (1912), 809, 1468.



(VII) 1,4-*Iso*propenyl*iso*propylene-Δ^1-tetrahydrobenzene (isomeric form of VI).

(VIII) 1,4-Di*iso*propenylbenzene (2 conjugated double bonds).

Re the sesquiterpene *d*-longifolene see p. 128 of this *Report*.

Alcohols.

Detection of Alcohols in form of their allophanates. — It is known that by the action of gaseous cyanic acid on primary and secondary alcohols, that allophanates are chiefly formed, together with small quantities of urethanes. A. Béhal[1]) also found that this reaction can be applied to tertiary alcohols. Phenols and terpene alcohols especially can be detected in this way.

In order to obtain the characteristic allophanates, gaseus cyanic acid is passed into the alcohol; the reaction product is washed with ether. After the excess alcohol and the urethanes produced have been separated, the residue is crystallised from hot alcohol, benzene, or acetone.

All the allophanates prepared by Béhal were crystalline odourless compounds, very slightly soluble in cold ether, and slightly soluble in cold alcohol. The allophanates of the tertiary aliphatic alcohols and of the phenols were saponified by boiling water with formation of CO_2, urea, and alcohol. Amongst the terpene alcohols, which otherwise behaved normally, linalool[2]) was an exception. Great exceptions to the rule[2]) were observed in the cyclic alcohols which contained phenol-groups. If the phenol groups were esterified, then the reaction proceeded normally.

Unsaturated alcohols in green plants. — Curtius and Franzen[3]) pointed out years ago that a mixture of unsaturated alcohols is present in the leaves of the hornbeam and edible chestnut. The following were identified in the hornbeam leaves: — butenol, pentenol, hexenol, an alcohol $C_8H_{14}O$, and one or more higher alcohols; in the chestnut leaves: — lower homologues of hexenol, hexenol itself and higher unsaturated alcohols. There is also a mixture of similar composition present in the oak *(Quercus sessiliflora)*.

Now the smell of the alcohol mixture from the three plants, especially on dilution, is exactly the same — a quite characteristic pleasant odour recalling to mind that of raspberries, tea, and roses. Franzen and Wagner[4]) made use of this characteristic sign — obtainable from 1 kg. or less of leaves — in order to examine 40 more plants for the presence of the mixture of unsaturated alcohols — elder, lime, wormwood, potato, strawberry, stinging nettle, birch, peppermint.

For this purpose they treated the freshly plucked, finely divided leaves with steam and baryta water to get rid of the volatile acids, and the distillate with silver oxide and caustic soda, which converted the aldehydes into the corresponding carboxylic acids. 50 cc. distillate contained the alcohol mixture.

The characteristic smell was identified with certainty in a total of 40 plants. Thus it can be assumed that, in all probability, this mixture of unsaturated alcohols is a normal constituent of green leaves.

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[1]) Compt. rend. **168** (1919), 945. — [2]) Further particulars wanting. — [3]) Cf. *Report* April **1915**, 80. — [4]) *Sitzungsber. der Heidelberg. Akad. der Wissensch. Math.-Naturw. Klasse. Abt. A 1920, 2. Abhandl.* Heidelberg **1920**.

In examining the mountain ash (*Sorbus Aucuparia*, L.) and the eagle fern (*Pteridium aquilinum*, Kuhn), the distillate smelled of prussic acid, which was identified by the Prussian-blue test. In both cases a glucoside may have been present, which split off prussic acid.

In strawberry leaves, an intense smell of lemons appeared, which indicated the presence of citral.

Since a large amount of oil-drops was noticed in the original distillate of various plants — the ivy amongst others — Franzen and Wagner assume that ivy yields an essential oil, about which nothing further is yet known.

Aldehydes.

Ch. Moureu and G. Mignonac[1]) give a process for the *preparation of aldehydes and ketones* from primary and secondary alcohols by catalytic oxidation. By means of silver nitrate and formaldehyde, silver was precipitated in a finely divided condition on asbestos, which was used as the catalyst. It was shown to be advantageous to first pass the alcohol vapour with an insufficient quantity of air over the catalyst heated to 230 to 300°. The reaction mixture was then exposed with the remainder of the calculated quantity of air to a second layer of the catalyst. There were produced: — From methyl alcohol at 360 to 400°, 62 per cent. formaldehyde, obtained from transformed alcohol, together with CO, CO_2 and hydrogen; from ethyl alcohol at 340 to 380° 89 per cent. acetaldehyde, CO_2 and CO; from *n*-butyl alcohol at 330 to 350°, 93 per cent. butanal; from amyl alcohol at 330 to 350°, 94 per cent. valeraldehyde; from allyl alcohol 70 to 75 per cent. acrolein; from benzyl alcohol at 300°, 80 per cent. benzaldehyde; from cinnamic alcohol at 300°, 60 to 70 per cent. cinnamic aldehyde; from *iso*propyl alcohol 90 per cent. acetone; from secondary butyl alcohol at 350 to 400° 90 to 96 per cent. methylethyl ketone.

We have already reported on a new universally applicable method of Rosenmund[2]), according to which, *aldehydes* can be prepared by the catalytic reduction of acid chlorides. According to A. Sonn and E. Müller[3]), the following process — starting from the imidochlorides — for preparing aldehydes is applicable to aromatic acids, and in many cases is to be preferred to the Rosenmund method. Since the chlorine in the imidochlorides is very easily exchanged for hydrogen by means of stannous chloride in ethereal solution, the tin double-salts of the Schiff bases can be easily obtained, and on heating these with dilute acids, the aldehyde may be produced.

Thus to obtain benzaldehyde, 70 g. (4 molecules) of dried stannous chloride are dissolved in 350 cc. of water-free ether by passing in hydrochloric acid gas. 25 g. (1 molecule) of freshly prepared benzanilide-imidochloride $C_6H_5 \cdot C \cdot Cl : N \cdot C_6H_5$ in 200 cc. of dry ether are added to the above solution, when the crystalline, lemon-yellow tin double salt is gradually precipitated $(C_6H_5CH : NC_6H_5)(HCl, SnCl_2)$. Treated with hydrochloric acid and steam-distilled, the salt is easily decomposed, and the yield of benzaldehyde is nearly quantitative.

Sonn and Müller similarly prepared the aldehydes of cinnamic acid, *p*-hydroxybenzoic acid and trimethyl ether gallic acid. The preparation of aldehydes from aliphatic acids did not succeed, probably because the commercial stannous chloride was not sufficiently pure.

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[1]) *Compt. rend.* **170** (1920), 258. As per *Chem. Zentralbl.* **1920**, I. 526. — [2]) *Report* **1918**, 122. — [3]) *Berl. Berichte* **52** (1919), 1927.

The reaction between *aldehydes* and *acid halides*, which is only occasionally mentioned in literature[1]), has been searchingly studied by R. Adams and E. H. Vollweiler[2]). From their experiments it appears that the reaction is a general one. Benzoylbromide, benzoylchloride, a number of their substitution products, and oxalylbromide were condensed with various aromatic aldehydes, *e. g.*, benzaldehyde, anisaldehyde, terephthalic aldehyde, acetylvanillin, piperonal, methylsalicylaldehyde, methylvanillin, cinnamic aldehyde and furfural. Addition products were formed from one molecule of acid haloid and one molecule — in the case of oxalylbromide 2 molecules — of aldehyde, of the general formulæ $RCHXO \cdot CO \cdot R'$ and $R \cdot CHXO \cdot CO \cdot COOCHXR'$ (X = halogen).

The correctness of these formulæ is proved by the reaction product of benzoylbromide and benzaldehyde chosen as an example. In consideration of the comparative instability of this compound, and that in several cases it behaves as a mixture of aldehyde and halide, one or other of the following formulæ may be assigned to it.

$$\underset{\text{(I)}}{C_6H_5CH\begin{matrix}O\\ \diagup\\ \diagdown\\ O\end{matrix}CBrC_6H_5}; \quad \underset{\text{(II)}}{C_6H_5C(OH)BrCOC_6H_5}; \quad \underset{\text{(III)}}{C_6H_5CHBrOCOC_6H_5}.$$

The first formula, given in "Beilstein" with the 4 linked-ring, is improbable, the second with an hydroxyl group and a halogen attached to the same carbon atom would be such an unstable compound that it could not be isolated. On the contrary, the third formula which represents the compound as an ether — phenylbromomethyl benzoate, should be the correct one. If silver benzoate be caused to react with the compound, benzylidene benzoate is formed.

$$C_6H_5CHBrOCOC_6H_5 + C_6H_5COOAg = AgBr + C_6H_5CH(OCOC_6H_5)_2.$$

With water all halide-aldehyde compounds decompose more or less rapidly into the aldehyde, the organic acid and the halogen acid.

Cold absolute alcohol reacts very slowly with the phenylbromomethyl benzoate and forms in the course of 24 hours benzaldehyde, hydrobromic acid, and ethyl benzoate.

$$C_6H_5CHBrO \cdot COC_6H_5 + C_2H_5OH = C_6H_5CHO + HBr + C_6H_5COOC_2H_5.$$

Ammonia dissolved in dry ether splits the addition-compound at once into benzamide, benzaldehyde, and ammonium bromide. Aniline dissolved in dry ether, on the contrary, reacts quite differently with phenylbromomethyl benzoate. Phenylbromomethyl aniline and benzoic acid are produced, without in the least any splitting into benzaldehyde and benzoylbromide.

$$C_6H_5CHBrOCOC_6H_5 + C_6H_5NH_2 = C_6H_5CHBrNHC_6H_5 + C_6H_5COOH.$$

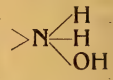
Accordingly the addition-compounds behave on the one hand as if they were merely a mixture of aldehyde and halide, on the other, however, they give quite characteristic reactions, which mark them as chemical compounds (esters).

In a treatise on the action of *ammonia* on *acetaldehyde* O. Aschan[3]) publishes his observations, which considerably enlarge our knowledge of the formation and constitution of aldehyde-ammonia. Aschan showed that the melting point stated in books — 70 to 80° — is too low, and that pure aldehyde-ammonia, which he obtained in a new way by means of concentrated aqueous ammonia, melts at 96 to 98°. From the cryoscopic molecular-weight determination in aqueous solution (molecular weight found

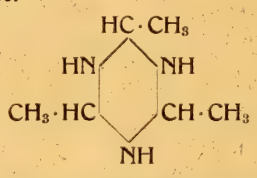
[1]) *Berl. Berichte* **17** (1884), 911; **42** (1909), 3066; **46** (1913), 1425. — [2]) *Journ. Americ. chem. Soc.* **40** (1918), 1732. — [3]) *Öfversigt af Finska Vetenskaps-Societetens Förhandlingar* **57** (1914/15). *Afd.* A, No. 14.

164.2) it appeared that in freshly dissolved aldehyde-ammonia a structure is present, which consists of 3 molecules of the simple compound C_2H_7NO with the inclusion of more or less water of hydration. If the solution of the compound is allowed to stand 24 hours or more, then a new body with the molecular weight of 126 appears, which corresponds to that of the bimolecular aldehyde-ammonia $(CH_3CH{=}NH)_2 \cdot 2H_2O$. Hence the trimolecular molecule, which is present in the solution at the commencement, gradually decomposes into the bimolecular molecule of aldehyde-ammonia. This fact speaks against the assumption of Delépine[1]), that the stable, heterocyclic triethylidene-imine ring (I) is present in the solid compound melting at 95 to 97°.

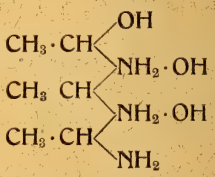
Aschan rather assumes, that the individual C_2H_7NO groups hang together in open chain (II) by means of the nitrogen atom. The ease with which the trimolecular aldehyde-ammonia disintegrates in acids and its reaction with certain compounds as simple aldehyde-ammonia (formation of alanine, dihydropyridine compounds), supports this assumption.

Also the occurrence of the hypothetical ammonium group  explains the easy disintegration of the structure into single molecules.

As by-product in the preparation of aldehyde-ammonia, according to the older method known, a new compound was obtained — dihydroxytriethylidenediimine, m. p. 45 to 47°, which represents a condensation product of the bimolecular aldehyde-ammonia with aldehyde.



(I) 2, 4, 6-Trimethylhexahydro-1, 3, 5-triazine (aldehyde-ammonia after Delépine).



(II) Common trimolecular aldehyde-ammonia after Aschan.

Re action of benzyl alcohol, *benzaldehyde* and benzyl ester on helminthes see p. 66 of this *Report*.

Ketones.

After C. Neuberg had successfully accomplished the *phytochemical reduction of methylheptenone* to methylheptenol[2]), he and F. F. Nord[3]) succeeded in reducing, by biochemical means, other ketones of the aliphatic and also of the aromatic series to the corresponding secondary alcohols. In this manner he obtained from methylethyl-ketone, secondary *n*-butyl alcohol; from methyl-*n*-propylketone, methyl-*n*-propylcarbinol; from methyl-*n*-hexylketone, secondary octyl alcohol; from methylnonylketone, methyl-nonylcarbinol; and from acetophenone, methylphenylcarbinol. Whilst aldehydes, which Neuberg likewise reduced by means of yeast, appear in the animal and vegetable kingdom as intermediate links in important metabolic processes, nothing is known about ketones — acetoacetic acid excepted — beyond the fact that they are of importance in metabolism. Ketones indeed, are widely spread in nature, but only rarely are the corresponding secondary alcohols met with[4]).

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[1]) *Compt. rend.* **128** (1899), 105. — [2]) Cf. *Report* **1919**, 140. — [3]) *Berl. Berichte* **52** (1919), 2237. — [4]) Methylheptylcarbinol and methylnonylcarbinol occur in rue oil, and in the volatile coconut oil; methyl-heptylcarbinol in oil of cloves; 2-methylheptene-2-ol-6 in linaloe oil. Cf. *Report* April **1911**, 55; Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 351; vol. II, p. 481.

Neuberg, as in earlier experiments, reduced the ketones with yeast, which was required in greater quantities than usual. Also only a yield of 10 per cent. of secondary alcohols was obtained. The reaction products, which could be isolated by treatment of the unchanged ketone with sodium bisulphite or hydrazine bases, were regularly optically active, and were mostly dextrorotatory. In no case were optically-pure alcohols formed; for example, the rotation shown by methylethylcarbinol (prepared from methylethylketone) ($[\alpha] + 3.34°$), was considerably higher than what R. Meth found for the secondary butyl alcohol ($[\alpha]_D + 0.32°$) which he had obtained by splitting the corresponding butylsulphuric acid by the alkaloid salt method. The fact that the ketones may be reduced to optically active secondary alcohols, proves that a true reduction process occurs, and possibly not a rearrangement in alcohol and acid. Since in all cases, as in the reduction of methylheptenone, considerable quantities of acetaldehyde appeared, it is to be assumed that during the course of the reaction, it is a case of relationship between phytochemical reduction and carbohydrate metabolism.

Optically active alcohols are also obtained when racemic carbinols are decomposed by fungus cultures. Whilst here, however, an antipode is removed by oxidation, Neuberg gets the alcohol by reduction of the ketone. Here the stage of the inactive form is not passed through; a carbinol appears that is richer in the optically active component than one obtained by the decomposition of racemic alcohols.

Further the question was of interest, whether also compounds with more carbonyl groups in the molecule, as diketones, could be biochemically hydrogenized[1]). It was found that diacetyl $CH_3COCOCH_3$, by the action of living yeast could be very easily converted into lævorotatory 2,3-butylene-glycol $CH_3CHOHCHOHCH_3$, with a yield of 35 per cent. This result is not so surprising, when it is considered that diacetyl occurs in the volatile oils of higher plants, *e. g.* in savin, cypress oils, &c.; the diketone also is of importance in the metabolic processes of innumerable micro-organisms.

This leaves the question undecided whether the reduction of diacetyl passed through the stage of the semihydrated diketone acetylmethylcarbinol; but according to the behaviour of benzil $C_6H_5COCOC_6H_5$, it may be assumed to do so. Benzil, when biochemically reduced, yielded chiefly benzoin $C_6H_5CHOHCOC_6H_5$, but no hydrobenzoin. Smaller quantities of an optically active substance, probably *l*-benzoin, were attached to the benzoin. In the reduction of the diketone also, in addition to the reaction products, an increased formation of acetaldehyde was demonstrated.

By means of aniline-zinc-chloride $ZnCl_2(NH_2C_6H_5)_2$, that had formerly been pointed out to act as a condensation agent between ketones and amines[2]), G. Reddelien and O. Meyn succeeded in obtaining condensation products of hydroaromatic ketones with aniline and aniline derivatives as per method of Schiff's bases[3]).

*Cyclo*hexanone heated for 20 minutes at 155° with aniline and a little aniline-zinc-chloride, gave a bright yellow oil of boiling point 140°, *cyclo*hexanoneanil $C_6H_{10}:NC_6H_5$. The oil easily changes by autocondensation into *cyclo*hexylidene-2-*cyclo*hexanoneanil $C_6H_{10}:C_6H_8:NC_6H_5$, which is also obtained as chief product if the reaction between *cyclo*hexanone, aniline and aniline-zinc-chloride is allowed to continue for a longer time (45 minutes) at 180°. Analogously menthone with aniline yielded menthoneanil, a yellow oil (b. p. 159 to 160° at 12 mm); with *p*-toluidine, menthone-*p*-toluil, a yellow oil (b. p. 178° at 16 mm); with *p*-anisidine, menthone-*p*-anisil (white crystals, m. p. 61.5°). All these compounds were quickly oxidized in the air, and became dark coloured.

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[1]) *Berl. Berichte* **52** (1919), 2248. — [2]) *Berl. Berichte* **43** (1910), 2476. — [3]) *Berl. Berichte* **53** (1920), 345.

Amongst the unsaturated hydroaromatic ketones, pulegone yielded a normal anil, a yellow oil (b. p. 148 to 150° at 13 mm.), and in addition varying amounts of two other compounds, which were regarded as addition products of aniline and pulegone and pulegoneanil. Pulegone has a pair of conjugated double bonds >C:C·C:O, and it is known that by the action of an amine on such a system, the amine is frequently added on with rupture of the double bond. A complete splitting of pulegone-anil into 2-methyl-*cyclo*hexanoneanil and acetoneanil was, however, not observed. In contrast to pulegone, dihydrocarvone and carvone yielded anils (yellow oils, b. p. 170 to 171° at 15 mm. and b. p. 180 to 182° at 17 mm.) without the formation of noteworthy by-products. With aniline hydrochloride as condensing agent camphoranil was obtained, a bright yellow, almost odourless oil (m. p. 13.5°, b. p. 164.5 to 166° at 15 mm.). It was quickly split up into camphor and aniline by dilute acid.

The anils of the unsaturated hydroaromatic ketones in sulphuric acid solution give a deep blue coloration with nitric acid, the same with nitrites, chlorates, chromates and hydrogen peroxide. *Cyclo*hexanoneanil, menthoneanil and camphoranil, show no, or else a very slight coloration.

G. Reddelien[1]) has obtained *condensation products of benzophenone* with p-*aminoazobenzene*, by heating benzophenone-anil $(C_6H_5)_2C = NC_6H_5$ with *p*-aminoazobenzene in the presence of some aminoazobenzene hydrobromide at 170 to 180°, and then further heating in vacuum to 230°. The resulting diphenylmethylene-*p*-aminoazobenzene, m. p. 123°, was a magnificent crystalline orange-yellow substance possessing strong dichroism. Analogously, the diphenylenemethylene-*p*-aminoazobenzene (m. p. 141—142°, orange-coloured needles also strongly dichroic) was produced from fluorenoneanil. In addition, Reddelien prepared a few aldehyde-*p*-aminoazobenzenes.

As with the ketone anils, the salt formation of these compounds was accompanied by phenomena of halochromism. The halochromism was intensified if the C:N group was conjugated with a neighbouring C:C group, such as with cinnamylideneaminoazobenzene.

Thujone.—By reduction of sabinol with sodium in amylalcoholic solution Semmler obtained an alcohol, which on oxidation yielded a *β*-thujone, which was not further characterized[2]). If sabinol is reduced in another way, a lævorotatory thujone can be obtained from the alcohol. Wallach[3]) caused free hydrogen to act on sabinol in the presence of palladium chloride and obtained, in addition to hydrocarbons, a lævorotatory secondary alcohol, which on careful oxidation yielded chiefly *l*-thujone. The ketone had the following properties:— b. p. 203 to 205° at ordinary pressure, $d_{20°}$ 0.907, $[\alpha_D]$ — 30.62° (16 per cent. solution in methyl alcohol); n_D 1.4507.

Since its rotatory power considerably exceeds that of a previous preparation obtained from thuja oil (α_D — 10.23°)[4]), it must still remain undecided whether a third modification of thujone is present, whose existence had already been earlier indicated, but has not yet been proved. The above preparation yielded a fluid oxime, which on long standing showed signs of crystallising, by the appearance of slight deposits, but which also contained small quantities of *β*-thujone.

Thujone-containing oils, which have been kept for a long time, show a greater or less content of *α*-thujaketonic acid $C_{10}H_{16}O_3$. This acid was identified in old stocks of sage oil, and in fractions consisting essentially of thujone of: — thuja, tansy, worm-

[1]) *Berl. Berichte* **53** (1920), 340. — [2]) Cf. *Report* October **1900**, 73. — [3]) *Nachr. K. Ges. Wiss. Göttingen* **1919**, meeting of July 18th, p. 10. — [4]) Cf. *Report* April **1905**, 111.

wood and artemisia oils. From 0.6 kg. tansy oil, kept in a large flask, Schimmel & Co. were able to obtain 14 g. of the acid by shaking up with caustic soda solution. A very long kept tanacetone gave 11 per cent. (by volume), and a thrice-distilled fraction from thuja oil, boiling point 200 to 212°, gave 20 per cent. (volume) of acid ingredients, mostly α-thujoketonic acid after treatment with caustic soda solution. If a perfectly satisfactory explanation of the formation of these ketonic acids cannot be furnished from experimental observations, then one may assume that thujone is prone to enolisation, and reacts as an unsaturated compound (VIII, see p. 138 of this *Report*). Probably this is the reason why it is so easily attacked by potassium permanganate.

The facts observed may be employed in testing old stocks of essential oils for thujone. The preparations are shaken up with caustic soda solution, the acid is then tested for its thujaketonic acid content according to Wallach's directions.

Pulegone sulphonic acid.—It has been long known that pulegone (I) forms with an aqueous solution of SO_2, a sulphonic acid which is very easily soluble in water. Wallach[1]) has made a thorough examination of this pulegone sulphonic acid. Whilst the acid is obtained as an almost colourless syrup, which decomposes over concentrated sulphuric acid with darkening and the splitting off of sulphurous acid and pulegone, the well crystallised salts of pulegone sulphonic acid are remarkable for their great stability. If the aqueous solution of the barium salt of the sulphonic acid be warmed with bromine, no precipitation of barium sulphate takes place. This fact speaks for a firm linking of the sulphurous acid radicle. Also all the salts behave as saturated compounds in the permanganate test. From this, the salts of pulegone sulphonic acid correspond by no means with the salts obtained by the addition of sodium bisulphite to saturated ketones, so that it is rather to be assumed that the sulphurous acid adds on to the semicyclic linking. As the salts do not correspond to the simple formula $C_{10}H_{17}O \cdot SO_3M$, and since they all contain water firmly bound, it may almost be assumed that the carbonyl group takes part in the taking up of the water.

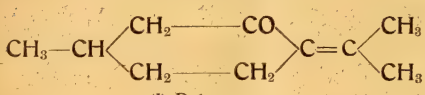
Of great interest was the question—which conditions favour the additive power of sulphurous acid to pulegone, and to the similarly behaving camphor phorone (II). Is the tertiary semicyclic carbon linking alone decisive for the additive power; are semicyclic linkings completely endowed with this property, or, in the cases named, is the juxtaposition of the carbonyl group or of other acid-containing groups to the double linking of the carbon atoms the cause?

From the behaviour of sabinol (III) it could be shown that the first question can in all probability be answered in the affirmative. The chief reaction product between sabinol and sulphurous acid—apart from a neutral compound of m. p. 147 to 148°—was a light and well crystallising sulphonic acid of the formula $C_{10}H_{15}SO_3H$ (m. p. 98 to 99°), whose formation took place with the elimination of one molecule of water. This acid behaved as a strongly unsaturated compound both with permanganate and bromine. The question now arose whether this easy additive power was decided by the presence of the menthene bond, or by the ease with which the 3-ring may be broken. From the behaviour of the reduced sabinol, *i. e.*, thujyl alcohol (IV), it appeared that after the breaking up of the semicyclic double bond, the additive power for sulphurous acid completely disappeared. On the other hand the 3-ring remained intact in the sulphonic acid, for on being treated with caustic potash solution thujone (V) could be obtained. No breaking up of the tricyclic ring resulted on the generation of an ethylene linkage,

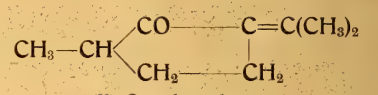
[1]) *Nachr. K. Ges. Wiss. Göttingen* **1919**, meeting of July 18th, p. 1.

as in the transformation of thujone into carvotanacetone or *iso*thujone. In this case the formation of a *di*hydrocymene sulphonic acid, corresponding to formula III, ought to have been possible, which would have had the tendency to split off sulphurous acid with formation of cymene. However, the formation of cymene was never observed. Otherwise an acid of formula VII, formed by the transformation of sabinol with sulphurous acid, would indicate and easily explain the origin of thujone from the sulphonic acid. Still the constitution of pulegone sulphonic acid cannot yet be regarded as incontestably established, for acid VII, contrary to its accepted formula, yielded no α-thujaketonic acid on oxidation with permanganate.

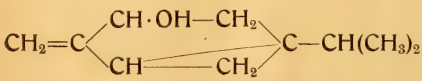
The great readiness with which sabinol reacts with sulphurous acid with the formation of well crystallising sulphonic acids, and the (under suitable conditions) remarkable insolubility of the substance, will allow this body, so often occurring in volatile oils, to be easily identified.



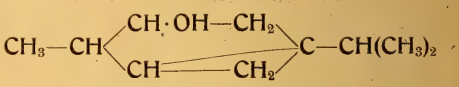
(I) Pulegone.



(II) Camphor phorone.

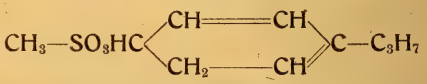


(III) Sabinol.

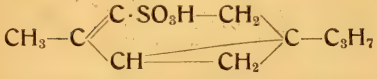


(IV) Thujyl alcohol.

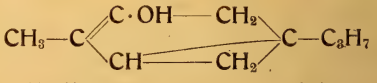
(V) Thujone.



(VI) Dihydrocymene sulphonic acid (is not formed).



(VII) Sulphonic acid of the isomeric sabinene.



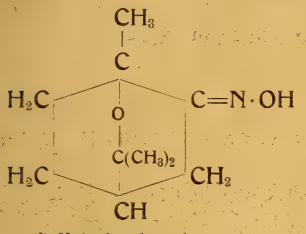
(VIII) Hypothetical enol-form of thujone.

Ketocineole.—Several years ago G. Cusmano[1]) described a ketone $C_{10}H_{16}O_2$ (ketocineole), whose method of preparation has recently been improved by him[2]). On warming terpineol nitrosochloride with 90 per cent. alcohol he obtained inactive ketocineole oxime (I), colourless rhombic crystals melting at 140°, which formed cineole-amine on reduction with sodium and boiling amyl alcohol. On treating the oxime with sodium nitrite and sulphuric acid a pernitroso compound (II) was obtained, which with concentrated aqueous ammonia yielded inactive ketocineole (III). The ketone melts at about 42°, is soluble in about 50 parts of water, easily soluble in organic solvents, and very easily volatile.

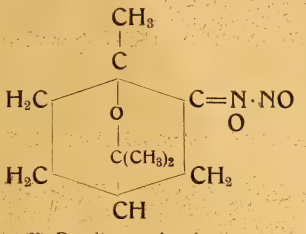
Similarly from *d*-terpineol nitrosochloride, active ketocineole oxime was obtained in prismatic crystals (m. p. 168°; $[\alpha]_{D10^\circ} - 11.8^\circ$ [4.72 per cent. solution in methylalcohol]) and from this a further active ketocineole in colorless, leafy crystals (m. p. about 50°; $[\alpha]_{D25^\circ} - 44.0^\circ$ [1.5 per cent. solution in water]) was obtained. The ketocineole, on oxidation with potassium permanganate in sulphuric acid solution, yielded homoterpenylic acid methylketone (IV); in alkaline solution cineolic acid (V). Accordingly

[1]) *Gazz. chim. ital.* **42** (1912), I. 1. — [2]) *Gazz. chim. ital.* **49** (1919), I. 26. As per *Chem. Zentralbl.* **1919**, III, 329; cf. also *Report* **1919**, 155.

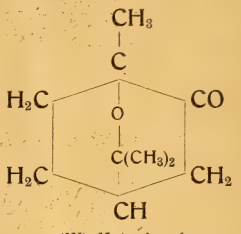
the ketone resembles camphor and pinocamphone in its behaviour, which likewise possess a bridge. Pinocamphone for example, yields on oxidation with potassium permanganate a ketonic acid (pinonic acid) together with the dibasic isomeric camphoric acids[1]). The rings of menthone, tetrahydrocarvone and thujone, on the contrary, which have no bridges, were only split up between keto group and tertiary or quaternary carbon atom. Ketocineole, which is very stable in the presence of dilute acids, is easily converted into dibromo-1,8-tetrahydrocarvone (VI)[2]) by ethereal hydrobromic acid.



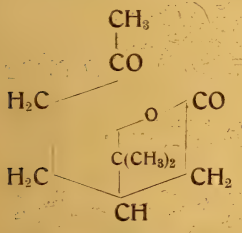
(I) Ketocineole oxime.



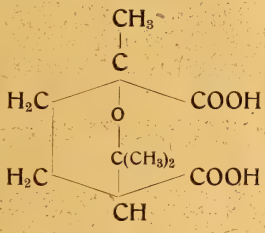
(II) Pernitroso cineole.



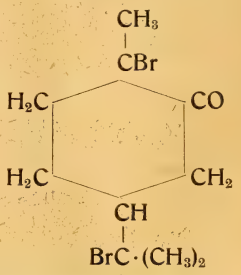
(III) Ketocineole.



(IV) Homoterpenylic acid methylketone.



(V) Cineolic acid.



(VI) Dibromo-1,8-tetrahydrocarvone.

In his researches on the reduction products of *hydroxymethylene camphor* and methylene camphor, H. Rupe[3]) never succeeded in finding the second form, which ought to have been formed during reduction in consequence of the freshly appearing asymmetric carbon atom (I). On the contrary, Rupe, M. Sieberth and W. Kussmaul[4]) showed that amino-methylene camphor (II), (III) and most of its derivatives can appear in two forms, in a low-melting and usually easier soluble β-form, and in a higher melting, and mostly more difficultly soluble α-form. With a few exceptions they can change from one form to the other (intramolecular rearrangement). Either both forms were equally stable, or when the one was more unstable than the other, it almost always happened to be the low-melting β-form. The two derivatives of anthranilic acid (IV) are especially interesting, for within quite small temperature differences one form is converted into the other. These intramolecular rearrangements occur spontaneously on keeping, by light, and by means of higher boiling solvents, &c.

Since a new asymmetric carbon atom does not appear, it is to be assumed that geometrical stereoisomerism is present (*cis-trans*-isomerism). A complete proof cannot yet be brought forward. Also no far-reaching conclusions could be drawn from the optical examinations difficult owing to the great insolubility of the aminocamphor derivatives, since the amount of material for observation was too small.

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[1]) *Liebig's Annalen* **346** (1906), 236. — [2]) Cf. also *Report* April **1915**, 105. — [3]) Cf. *Report* **1919**, 138. — [4]) *Helvet. Chim. Acta* **3** (1920), 50. As per kindly forwarded reprint.

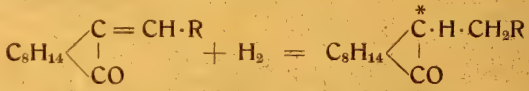
The preparation of hydroxymethylene camphor was improved by converting the greater part of the camphor into the sodium compound by means of sodium amide in benzene solution.

The yield from 100 g. camphor amounted to 70 to 75 g. as against 40 g. by the older method (with sodium in ether solution). α-aminomethylene camphor (m. p. 156°) was changed into the very unstable β-form (m. p. 103 to 104°) by distillation under reduced pressure.

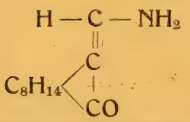
Both forms of benzoylamidomethylene camphor were simultaneously produced on treating amidomethylene camphor with benzoylchloride and pyridine; the α-form (m. p. 208°) was obtained alone by condensation of hydroxymethylene camphor with benzamide. The α-form could be quantitatively changed into the β-form (m. p. 112°) by boiling with pyridine; and the β-form converted completely into the α-form by the action of ultraviolet light.

Further, the following derivatives were prepared, and similarly examined:—Methylene camphor-*p*-nitranilide, α-form (m. p. 180 to 181°), β-form (m. p. 151 to 152°); methylene camphor-*p*-phenylene diamine (m. p. 153 to 154° and m. p. 163°); methylene camphor-*p*-phenetidine, β-form (m. p. 111 to 112°), α-form (m. p. 166 to 167°); dimethylene camphor-*p*-phenylene diamine (m. p. 276 to 277°); methylene camphor diethylamine (b. p. 171.5 to 174° at 9 mm.); methylene camphor piperidine (b. p. 203 to 204° at 11 mm.); methylene camphor-tetrahydroquinoline (b. p. 118 to 120° at 11 mm.), methylene camphor urea (m. p. 197°); methylene camphor ethylurethane, α-form (m. p. 162), β-form (b. p. 175° at 9 mm.); condensation product of methylene camphor and anesthesine, α-form (m. p. 176°), β-form (m. p. 105°); condensation product of methylene camphor and arsanilic acid, decomposition at about 220° (m. p. 250°, indistinct); methylene camphor-anthranilic acid (IV), α-form (m. p. 176°), β-form (m. p. 112°).

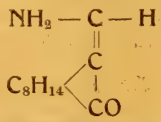
On treating the last-named compound with acetic anhydride and phosphorus oxychloride methylene camphor-*N*-acetylanthranilic acid (m. p. 185°) (V) and the β-lactame (m. p. 165°) (VI) were obtained.



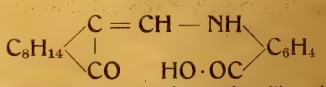
(I) Reduction of methylene camphor derivatives.



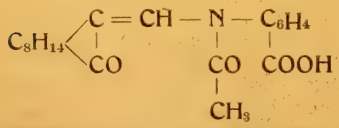
(II) Aminomethylene camphor trans (α)-form.



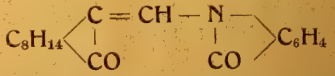
(III) Aminomethylene camphor cis (β)-form.



(IV) Methylene camphor-anthranilic acid.



(V) Methylenecamphor-N-acetylanthranilic acid.



(VI) β-Lactame of methylene camphor-anthranilic acid.

Phenols and Phenol Ethers.

E. E. Reid recommended *p*-nitrobenzylbromide for *identifying phenols*, and has prepared several ethers with this compound[1]). By the same process[2]), reid further obtained the *p*-nitrobenzyl ethers of the following phenols:—that of *o*-nitrophenol (m. p. 130°); that

[1]) Cf. *Report* 1918, 92. — [2]) *Journ. Americ. chem. Soc.* 42 (1920), 617.

of *p*-nitrophenol (m. p. 187.4°); that of 2,4-dinitrophenol (m. p. 248°); that of *o*-chlorophenol (m. p. 100°); that of *p*-chlorophenol (m. p. 101.3°); that of 2,4,6-tribromophenol (m. p. 163.5°); that of guaiacol (m. p. 63.5°); that of *α*-naphthol (m. p. 140°); that of *β*-naphthol (m. p. 106.5°); that of salol (m. p. 87°); that of methyl salicylate (m. p. 128.2°); that of ethyl salicylate (m. p. 125°); that of butyl salicylate (m. p. 92°); that of *o*-cresyl salicylate (m. p. 142.5°); and that of *m*-cresyl salicylate (m. p. 118°).

The ethers were best obtained from their corresponding alcohols. In preparing the ether of salicylic acid excess of alkali must not be present, as is permissible in all other cases.

H. D. Gibbs and M. Phillips discovered the most suitable means of obtaining *carvacrol* from *p*-cymene sulphonic acid[1]). They obtained the best results (74 per cent. of the theoretical yield), when they heated for 6 hours in autoclaves to 350°, the sodium derivative of *p*-cymene sulphonic acid (1 molecule) and sodium hydroxide (2.2 molecules). If water was added to the melt, the time had to be lengthened and the temperature raised. It is important to use autoclaves, for the deleterious influence of the atmospheric oxygen is thereby diminished; and nothing can be lost during the melting process. Only 60 per cent. of the theoretical yield was obtained when open vessels were used.

Amongst cymene derivatives p-*aminocarvacrol* is very suitable for the preparation of photographic developers. Comparative experiments showed that this compound is to be preferred to *p*-aminophenol as a developer, but that it is inferior to monomethyl-*p*-aminophenol (metol) and *p*-aminocresol. The isomeric *p*-aminothymol does not give so good results as the carvacrol derivative[2]).

Acids and Esters.

C. Marie, R. Marquis and Birckenstock have succeeded in *electrolytically reducing phenylacetic acid* to the corresponding alcohol[3]). Up to now only aromatic organic acids, such as benzoic acid and its derivatives could be reduced in this way. Oxalic acid, the one aliphatic compound, which by means of electrolysis is easily transformed into glyoxylic acid, is an exception in virtue of its structure.

Since an attempt to reduce phenylacetic acid according to Mettler's method[4]) failed, the alcohol was omitted, according to Tafel[5]), and very concentrated sulphuric acid (60 to 75 per cent. strength) was used.

Besides 15 gm. of recovered acid, the phenylethyl ester of phenylacetic acid was obtained, from which 1.65 gm. phenylethyl alcohol was won, corresponding to 33 per cent. of the transformed acid, according to the following conditions:—

Cathode liquid, 75 gm. concentrated sulphuric acid, 25 gm. water, 1 gm. gelatine, 20 gm. phenylacetic acid; area of lead cathode 100 sq. cm.; current intensity 10 ampères; duration of electrolysis 4 hours; 11 gm. sulphuric acid were added to the liquid every half hour.

A part of the alcohol produced by the electrolysis formed an ester with the sulphuric acid, only to be again electrolytically decomposed. If the yield was indeed small with this method, it furnished the proof that aliphatic acids also can be electrolytically reduced.

Cinnamic Acid.—By a series of exhaustive experiments E. Erlenmeyer and G. Hilgendorff[6]) proved the existence of *optically active cinnamic acids*, which were formed under the influence of the power emitted from asymmetric molecules (asymmetric induction). In their latest paper[7]) on optically active cinnamic acids, and the cinnamates of

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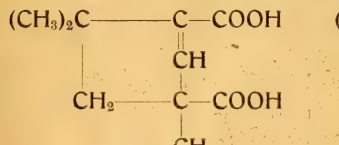
[1]) *Journ. Ind. Eng. Chem.* **12** (1920), 145. — [2]) *Journ. Ind. Eng. Chem.* **11** (1919), 455. — [3]) *Bull. Soc. Chim.* IV. **26** (1919), 512. — [4]) *Berl. Berichte* **38** (1905), 1745; **41** (1908), 4148; *Report* April **1909**, 129. — [5]) *Berl. Berichte* **33** (1900), 2214. — [6]) Cf. *Report* **1916**, 133. — [7]) *Biochem. Zeitschr.* **103** (1920), 79.

tartaric acid also formed during the production of the former, the authors bring forward further proofs that the activity of their preparations is caused solely and alone by the asymmetric configuration of the cinnamic acid molecule. For this purpose the constituents in the colloidal cinnamate mixture of the various melts of tartaric acid with cinnamic acid chloride, cinnamic anhydride, and cinnamic acid, obtained at 168 to 170°, were separated and more closely determined by ascertaining their carbon content and rotatory power. From the anhydride melt they succeeded in obtaining cinnamic acid preparations with rotatory powers up to $[\alpha] -9°$, together with a colloidal cinnamate mixture insoluble in ligroin with a rotatory power of nearly 100°. In contrast with this only 2 to 3° rotating cinnamic acid could be got from the chloride melt, although very highly rotating dicinnimate ($[\alpha]_D -275°$) was plentifully present.

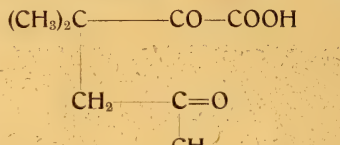
The authors emphasise that this state of affairs once again refutes the objection that the activity of the cinnamic acid preparations could be caused by the cinnamate mixed with them, and prove that as a matter of fact, asymmetric cinnamic acid molecules had been formed in the melts investigated.

Dehydroisofenchoic Acid.—A work by N. J. Toivonen[1]) gives an explanation of a series of peculiar reactions in the oxidation of dehydro*iso*fenchoic acid (I). In it the active components of the *d.l*-dehydro*iso*fenchoic acids, which previously had not been prepared, are also described.

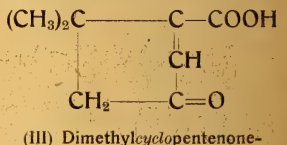
The product obtained after oxidising the unsaturated dehydro*iso*fenchoic acid with alkaline permanganate solution was itself unsaturated, hence it could not be the first oxidation product. This had changed in course of time, and the alkalinity of the oxidising liquid was the cause of this change. If one proceeds as ordinarily, by adding



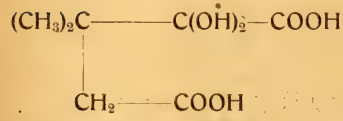
(I) Dehydro*iso*fenchoic acid.



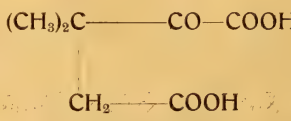
(II) α,δ-Diketo-β,β-dimethyl-caproic acid.



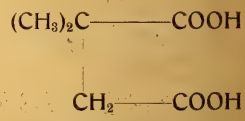
(III) Dimethyl*cyclo*pentenone-carboxylic acid.



(IV) α,α-Dihydroxy-β,β-dimethyl-glutaric acid.



(V) α-Keto-β,β-dimethyl-glutaric acid.



(VI) α,α-Dimethylsuccinic acid.

the permanganate solution drop by drop to the sodium carbonate solution of the dehydro*iso*fenchoic acid, till the colour stays; then a well-crystallising unsaturated acid of the composition $C_8H_{10}O_3$ (III) is obtained. The first oxidation product of dehydro*iso*fenchoic acid, the saturated, viscid α,δ-diketo-β,β-dimethylcaproic acid $C_8H_{12}O_4$ (II), can be obtained if a plentiful supply of CO_2 is passed into the solution during oxidation, or by mixing it with a sufficient amount of aluminium sulphate, and slightly acidifying immediately after oxidation. By the action of alkalies the acid $C_8H_{12}O_4$ changes into the already mentioned dimethyl*cyclo*pentenone-carboxylic acid $C_8H_{10}O_3$ (III). This on further oxidation with alkaline permanganate yields the α,α-dihydroxy-β,β-dimethyl-glutaric acid $C_7H_{12}O_6$ (IV) and the α,α-dimethylsuccinic acid $C_6H_{10}O_4$ (VI). Also on

[1]) *Liebig's Annalen* **419** (1919), 176.

oxidising with fuming nitric acid, as also in the potash-melt, the first-named acid, which gives off water in the vacuum desiccator with formation of α-keto-β,β-dimethyl-glutaric acid (V), is converted into the acid $C_6H_{10}O_4$.

Preparation of Organic Borneol Esters. — The weak solubility in acids of the material to be esterified, which renders the preparation of organic borneol ("camphol") esters from camphene or pinene hydrochloride so difficult, has, according to A. Dubosc[1]), been removed, by adding sulpho compounds, sulphoricinic acid in preference to all others. The sulphonic acid itself does not enter into the reaction; after separation of the acids, the borneol ester obtained is converted into borneol by saponification.

From the black-lye of the sulphate-cellulose manufacture O. Aschan and K. E. Ekholm[2]) were able to isolate a new body, *pinabietic acid* $C_{20}H_{30}O_2$. This resin acid (m. p. 176 to 178°) crystallises in glittering needles, and when dissolved in chloroform and acetic anhydride, gives a purple-red coloration with a little concentrated sulphuric acid, changing into violet, blue, and finally black. The optical rotatory power depends on the solvent, with which the acid probably forms additive compounds.

Re action of benzyl alcohol, benzaldehyde and *benzyl ester* on helminthes, see p. 66 of this *Report*.

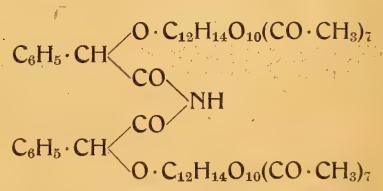
Glucosides.

G. Zemplén[3]) prepared several new acylated cellobiosides, heptacetyl-benzylcello-bioside, heptacetyl-methylcellobioside, heptacetyl-*iso*butylcellobioside and heptacetyl-phenylcellobioside, in order to isolate from them, by treatment with hydrobromic acid in glacial acetic acid solution, the crystalline acetylbromocellobiose (m. p. 190°, $\alpha_{D20°}$ +92°). In these experiments he proved that the glucoside bond is broken, but that the disaccharide, however, is not hydrolysed. The cleavage ensued as follows: —

$$\underset{\text{Heptacetyl-benzylcellobioside}}{C_6H_5CH_2\cdot O\cdot C_{12}H_{14}O_{10}(CO\cdot CH_3)_7} + 2\,HBr \rightarrow C_6H_5CH_2Br + H_2O + \underset{\text{Acetobromocellobiose}}{C_{12}H_{14}O_{10}(CO\cdot CH_3)_7Br}$$

The same treatment in the case of amygdalin led to no result. It follows from this, that by the presence of the nitrile group, the glucoside linking between the nitrile of mandelic acid and the biose becomes stronger than the ether bond between the two glucose radicles.

Further experiments led to the obtaining of a tetradeca-acetyl-di-amygdalinic acid imide (I) (m. p. 212°; $\alpha_{D21°}$ −72.1°), which was obtained by the action of hydrochloric acid gas on heptacetyl-amygdalin.



(I) Tetradeca-acetyl-di-amygdalinic acid imide.

P. Karrer and H. Weidmann[4]) obtained the methyl ester of β-*d*-glucoside-*o*-salicylic acid by methylating the salicinic acid (I) earlier prepared by them with diazomethane. The ester showed other properties than the isomeric natural product gaultherin (II)[5]), especially in its behaviour with enzymes. Whilst gaultherin is split up by the enzyme gaultherase, but not by emulsin, the methyl ester of salicinic acid is decomposed by

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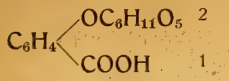
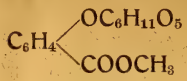
[1]) *Caoutchouc et Guttapercha* **15** (1920), 9555. As per *Chem. Zentralbl.* **1920**, I. 115. — [2]) *Finska Kemistsamfundets Meddelanden*. As per *Chem. Zentralbl.* **1919**, I. 285. — [3]) *Berl. Berichte* **53** (1920), 990. — [4]) *Helvet. Chim. Acta* **3** (1920), 252. — [5]) The glucoside gaultherin, from which methylsalicylate is obtained by fermentative splitting off, is present in the plant *Gaultheria procumbens*, L., in birch bark, in the roots of *Polygala* and *Spirwa* species, and in the cultivated pansy.

the latter. Hence it is to be assumed that gaultherin is an α-glucoside, and that the synthetically obtained ester belongs to the β-glucosides.

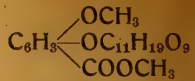


(I) β-*d*-Glucoside-*o*-salicylic acid.



(II) Gaultherin.

(III) β-*d*-Glucoside-*o*-2-hydroxy-4-methoxybenzoic acid.



(IV) Primverin.

They were further successful in preparing the β-glucoside of 2-hydroxy-4-methoxybenzoic acid (m. p. 163°) (III). The methyl ester of this compound is only distinguished by the sugar radicle from the primverin (IV)[1]), occurring in the roots of many *Primula* species.

The synthesis of the methyl ester of β-tetracetyl-glucoside-*o*-anthranilic acid (m. p. 165°) was also accomplished. The corresponding natural glucoside has hitherto not been found, but probably occurs in nature, since the methyl ester of anthranilic acid is contained in many volatile oils.

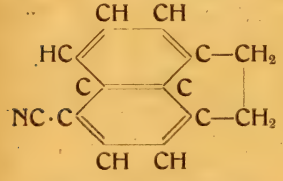
Nitrogenous Bodies.

The *action of cyanogen bromide on hydrocarbons and phenol ethers* in the presence of aluminium chloride has been studied by P. Karrer, A. Rebmann, and E. Zeller[2]). In general the nitrile was easily formed, as in the case of acenaphthene (I) and thiophene (II). *m*-tertiary butyl-toluene and naphthalene gave worse yields; acenaphthylene, indene and diphenyl formed no nitrile with cyanogen bromide and aluminium chloride.

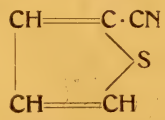
Cyanogen chloride can be used in place of cyanogen bromide for the synthesis; cyanogen iodide is to be less recommended, since much iodine is split off when using it.

If old, and hence probably polymerized, cyanogen bromide is used, instead of fresh, no monomeric nitrile is obtained, but polymeric compounds. Benzene, for example, when treated with old cyanogen bromide yielded the trimeric kyaphenine (III), but not benzonitrile.

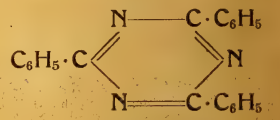
From phenol ethers, which gave still better results than the hydrocarbons, the cyanides of the following compounds were prepared: — of phenetol, α-naphthol-ethyl ether, neroline, veratrole, pyrogallol trimethyl ether, resorcinol dimethyl ether, hydroquinone



(I) Acenaphthene cyanide



(II) α-Thiophene cyanide (α-thiophenecarboxylic acid nitrile).



(III) Kyaphenine.

dimethyl ether. On saponifying 1-cyano-2-methoxy-naphthalene with caustic potash solution the related carboxylic acid was not obtained, but solely its amide. The reason probably is, that the CN-group is sterically hindered through the occupation of the two *ortho*-positions. The CN-group was always found in the *ortho*- or *para*-position to other groups.

Along with the phenol-ether cyanides small quantities of hydroxy nitriles were also formed from the phenol-ether cyanides during the reaction, by the saponifying effect of the water-free aluminium chloride.

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[1]) Cf. *Report* April 1913, 85. — [2]) *Helvet. Chim. Acta* 3 (1920), 261; cf. *ibidem* 2 (1919), 89; *Report* 1919, 146.

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